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**Retention:** Permanent

## **Phosphate Mineral Source Evaluation and Zone-of-Influence Estimates for Sediment Contaminant Amendments at the TNX Outfall Delta Operable Unit (U)**

**Anna S. Knox, Daniel I. Kaplan, and Thong Hang**



**December 29, 2003**

Westinghouse Savannah River Company  
Savannah River Site  
Aiken, SC 29808



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## LIST OF ACRONYMS

Bdl	below detection limit
BP	Biological Phosphate
CEC	Cation Exchange Capacity
$D_{eff}$	Effective Diffusion Coefficient
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
$K_d$	Distribution Coefficient
na	not analyzed
NCA	North Carolina Apatite
Proc.	processed
RCRA	Resource Conservation and Recovery Act
RP	rock phosphate
SRS	Savannah River Site
TNX OD	TNX Outfall Delta
ZOI	Zone-of-Influence

## 1 EXECUTIVE SUMMARY

The TNX pilot-scale research facility released processed waste, containing elevated concentrations of several metals and radionuclides into an unlined seepage basin between 1958 and 1980. The contents of this basin have entered the nearby swamp, the TNX Outfall Delta (TNX OD), by subsurface and overland flow. Studies were conducted to evaluate whether sediment amendments could be used to reduce contaminant mobility and bioavailability. Previous studies showed that the addition of a phosphate mineral, apatite, and zero-valent iron, Fe(0), were effective at immobilizing a broad range of contaminants at the site (Kaplan et al., 2002). It is anticipated that the sediment amendments will be broadcast on the ground surface and backfilled into drilled 2 cm diameter x 15 cm deep holes spaced across the contaminated area. The amendments' zone-of-influence of these two application methods was conducted to permit treatment design. The objective of this study was to determine 1) which source of phosphate mineral is most suitable for sediment-contaminant stabilization, and 2) what is the extent of the zone-of-influence of applied apatite and Fe(0).

Nine commercially available phosphate minerals, representing >95% of the phosphate production in the country, were evaluated for solubility, concentration of trace metals, and leachability of trace metals. Processed and mined rock phosphate contain high total concentrations of arsenic (As), cobalt (Co), chromium (Cr), copper (Cu), and strontium (Sr); however, they did not exceed the Resource Conservation and Recovery Act (RCRA) toxicity characteristic leaching procedure (TCLP) limits. The use of stronger extractants indicated that these elements were very strongly bound by most apatite material; therefore, if they were applied to contaminated sediment at a rate sufficient for remediation, they would not pose an environmental risk. The biogenic apatite (fish bone) contained significantly lower metal impurities than processed and mined rock phosphate and was appreciably more soluble, i.e., it had a logK<sub>sp</sub> of -45.2 compared to -57.0 for the mined rock phosphate samples.

There are many phosphate sources that can safely and effectively be applied to the TNX OD. By combining biogenic and mined phosphate it will be possible to obtain a wide range of phosphate solubility, permitting rapid immobilization of contaminants, while at the same time providing a slow release of phosphate for continued sediment treatment. Addition of Fe(0) is known to be very effective at removing As, Cr, Co and other elements from the aqueous phase. Therefore, its application at the TNX OD could significantly immobilize these contaminants.

The ZOI of surface applied amendments (horizontally applied), and amendments backfilled into holes (vertically applied) were evaluated under field conditions. Additionally, vertical application of ZOI was tested in the lab. For the surface applied amendments in the 13-month field study, P from the biological apatite and from the mined apatite moved ~3 cm; and Fe from the Fe(0) treatment moved ~5 cm. Retardation factors were calculated and used to estimate the zone-of-influence at various intervals. To provide a measure of lateral movement of the P and Fe in the vertical treatments, field and laboratory data were collected and applied to diffusion equations (Fick's second law) to provide effective diffusion coefficients. Both sets of data were reasonably consistent, indicating that P from the

biological and mined apatite and Fe from Fe(0) would be expected to diffuse more than 5 cm after 10 years.

It will not be possible to apply Fe(0) with apatite to the contaminated sediment at the TNX OD because an iron-phosphate phase precipitates, greatly reducing the mobility, and therefore the zone-of-influence of iron and phosphate. If both amendments are deemed necessary, it would be best to apply them at different times.

## 2 INTRODUCTION

### 2.1 BACKGROUND

The TNX pilot-scale research facility released process waste into an unlined seepage basin between 1958 and 1980. The basin, referred to as the Old TNX Seepage Basin, was designed to contain wastewater until it could seep into the underlying sediments. It was anticipated that the sediment would then impede contaminant migration. The waste discharged to the Old TNX Seepage Basin included chromium, mercury, sodium, uranium and thorium. The basin contents have entered the nearby inner swamp by subsurface and overland flow; the overland flow is the result of draining operations and overflow of the basin during closure in 1981.

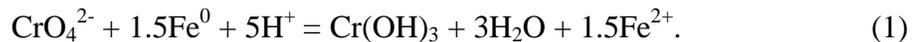
### 2.2 IMMOBILIZATION OF CONTAMINANTS BY PHOSPHATE AND FE(0)

Researchers have reported that apatite, a calcium-phosphate mineral, immobilizes lead (Pb) and other ions such as manganese (Mn), cobalt (Co), copper (Cu), cadmium (Cd), zinc (Zn), magnesium (Mg), barium (Ba), uranium (U), or thorium (Th) in contaminated media (Ma et al., 1995; Ryan et al., 2001; Seaman et al., 2001; Suzuki, et al., 1981; Suzuki, et al., 1982). Immobilization of these elements occurs due to precipitation, adsorption and isomorphic substitution. Wright et al. (1995) reported that the immobilization of Pb by apatite was primarily through a process of apatite dissolution followed by precipitation of various pyromorphite-type minerals under acidic conditions, or the precipitation of hydrocerussite [ $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$  or  $\text{Pb}(\text{OH})_2$ ] and lead oxide fluoride ( $\text{Pb}_2\text{OF}_2$ ) under alkaline conditions. Otavite ( $\text{CdCO}_3$ ), cadmium hydroxide [ $\text{Cd}(\text{OH})_2$ ], and zincite (ZnO) were formed in the Cd or Zn systems, respectively, especially under alkaline conditions. Phosphate-metal precipitates are typically very stable.

Suzuki et al. (1981 and 1982) concluded that the removal of Pb, Cu, Mn, Co, Cd, Zn, Ni, and Ba from contaminated medium was due not only to adsorption but also to an ion-exchange reaction between the cations in solution and the  $\text{Ca}^{2+}$  ions of the apatite. Suzuki et al. (1982) reported that the order of the ions according to the amount exchanged was as follows:  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Mn}^{2+} = \text{Co}^{2+}$ . In another paper, Suzuki et al. (1981) reported that the ranking of the ions according to amount exchanged was as follows:  $\text{Cd}^{2+}, \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Ba}^{2+}, \text{Mg}^{2+}$ . Data presented by Knox et al., (2003) are consistent with those of Suzuki et al. (1981, 1982), in that the apatite was more effective at reducing aqueous Pb than aqueous Co or Ba concentrations.

Isomorphic substitution is a process in which the contaminant substitutes for Ca, phosphate, or hydroxide in the apatite structure. This removal mechanism is highly desirable from the standpoint of contaminant stabilization because the contaminant becomes incorporated into the structure of the apatite. Isomorphic substitution is common in apatite because its crystalline structure is very flexible. Several different elements can substitute into its structure. Calcium exists in apatite in 7-fold and 9-fold coordination. The 7-fold coordinated Ca ions are about 10% smaller than the 9-fold coordinated ions. This difference in ionic radius permits a large range of contaminants to substitute for Ca, including the following constituents: Sr, Ra, Pb, Cs, Th, U(VI), and Cr(VI) (Deer et al., 1975). Elements that can substitute for phosphate (0.254 nm radius) include  $\text{TcO}_4^-$  (0.268 nm) and  $\text{CO}_3^{2-}$  (0.211 nm). Finally, the hydroxyl anion (0.153 nm) can be substituted with  $\text{Br}^-$  (0.196 nm),  $\text{Cl}^-$  (0.181 nm) and  $\text{F}^-$  (0.136 nm).

The other sediment amendment evaluated in this study was Fe(0). Fe(0) removes metals from the aqueous phase by three primary processes: reductive precipitation (by Fe(0) or Fe(II)), coprecipitation with Fe(II/III), and metal sorption by Fe(0)-originating, Fe(II/III)-oxyhydroxides. Reductive precipitation involves the transfer of electrons from Fe(0) to a constituent that is less soluble in the reduced than in the oxidized form. Common contaminants that can be removed from the aqueous phase in this manner are Cr, Hg, Mo, Tc, and U. For example, the reductive precipitation of Cr(VI) can be described by Equation 1:



In this example,  $\text{CrO}_4^{2-}$  is both more mobile and toxic than  $\text{Cr}(\text{OH})_3$ , which is predominantly in the solid phase.

As Equation 1 shows,  $\text{Fe}^{2+}$  ions are released and acidity is consumed during the reaction. Both of these changes are conducive to the formation of Fe(II/III)-oxyhydroxides. If other metals are present, they may coprecipitate with the Fe(II/III)-oxyhydroxide. Chrome removal by Fe(0) is believed to occur primarily through this reaction, whereby Cr,Fe(OH)<sub>3</sub> solid solutions are formed (Eary and Rai, 1987; Sass and Rai, 1987).

Fe(0) can remove aqueous contaminants by first oxidizing to form Fe(II/III)-oxyhydroxides, which then can act as a sorbent. The Fe(II/III)-oxyhydroxides increase the sorption capacity of the system. Contaminant removal in this manner is the least desirable of the three removal mechanisms due to the weak nature of the bond between the contaminant and the Fe(II/III)-oxyhydroxide.

### 2.3 PHOSPHATE ROCK – PHOSPHOROUS SOURCES

Phosphate rock minerals are the only significant global resources of phosphorus. The United States (U.S.) is the world's leading producer and consumer of phosphate rock. The southern states (Florida and North Carolina) and western phosphate fields (mostly Idaho and Utah) are the major mining areas in the U.S. Phosphate rock is produced by 11 companies at 18 mines; 12 mines in Florida and one in North Carolina accounts for 86% of domestic production.

Southern phosphate-rich deposits are of marine origin from Miocene and Pliocene ages, i.e., approximately 5-10 million years old. Biological and chemical changes transformed the phosphate that existed in the sea into the phosphate sediment that we mine today. There are many theories about how the Florida phosphate deposit was formed. One of the most common theories is that during the Miocene era, deep seawater currents flowed up onto topographically high areas. These upwelling currents caused nutrient and phosphate rich water to rise to the surface of the sea that covered Florida at the time. The phosphate precipitated from the seawater to form phosphate-rich sediment that solidified into nodules (Kohn et al., 2002). As time passed, sea levels dropped and phosphate and limestone were exposed as land. During the Pleistocene era, the marine phosphate deposits were geologically reworked and re-deposited in a concentrated form. Florida's phosphate deposit contains the teeth, bones and waste excrement from marine life and also the bones of terrestrial pre-historic animals such as mastodons, saber-tooth tigers, bears, camels, three-toed horses and other ancient animals.

The western phosphate deposits, Permian Phosphoria Formation, are older deposits that formed off the western shores of the Pangean super continent in what is today southeastern Idaho and surrounding states (Montana, Wyoming, Colorado, Utah, and Nevada). The Phosphoria Formation is considered a "super giant" among phosphate deposits, covering about 340,000 km<sup>2</sup> and containing five to six times more phosphorous than the total phosphorous budget in today's oceans (Knudsen and Gunter, 2002).

## 2.4 OBJECTIVE

The main objectives of this study were:

- 1) to determine which natural source of phosphate would be most suitable for remediating contaminated sediments (nine phosphate materials were tested),
- 2) to determine the Zone-of-Influence (ZOI) of two phosphate materials and Fe(0) in the TNX OD sediment under laboratory conditions, and
- 3) to determine the ZOI of two phosphate materials, Fe(0), and mixture of each phosphate material with Fe(0), applied horizontally or vertically, in the field (TNX OD).

Three types of phosphate sources were initially evaluated: mined rock phosphate (Florida, Idaho, North Carolina, and Tennessee), processed rock phosphate (North Pacific AG Products; Montana Natural Granulated Rock Phosphate, Spring Phosphate Powdered, and Volcanaphos) and a biogenic apatite (fish bones). Collected samples were analyzed for solubility, toxicity characteristic leaching procedure (TCLP), extractable metals, total elemental content and selective extraction metal content.

In the ZOI laboratory and field studies, two types of phosphate materials were tested: mined apatite from North Carolina and biological apatite (ground bones, reviewed at [www.pimsnw.com](http://www.pimsnw.com)), and zero-valent iron, Fe(0). Apatite is a common subsurface and surface sediment amendment for metal immobilization, whereas Fe(0) is not as commonly used for surface sediment applications as it is used for subsurface permeable reactive barriers.

### 3 MATERIALS AND METHODS

A detailed description of the laboratory and field procedure used in this study is presented in Appendix B: Work Instruction for the Laboratory Study and Appendix C: Work Instruction and Additional Results for the Field Study. The following is a brief synopsis.

#### 3.1 LABORATORY STUDIES

##### 3.1.1 Characteristics of Phosphate Sources

Nine phosphate materials (Table 1) were tested to determine which natural source of phosphate would be most suitable for remediation of contaminated sediments. The tested materials were collected from three sources of phosphate, mined rock phosphate (Florida, Idaho, North Carolina, and Tennessee), processed rock phosphate (North Pacific AG Products; Montana Natural Granulated Rock Phosphate, Spring Phosphate Powdered and Volcanaphos) and a biogenic apatite (fish bones) (Table 1). The collected samples were analyzed for pH, particle size distribution, organic matter content, solubility, toxicity characteristic leaching procedure (TCLP) extractable metals, and total elemental content. The phosphate material pH was determined from a 1:1 mineral/water equilibration solution (Thomas, 1996). Percent organic carbon was estimated by loss-on-ignition at a temperature of 375°C. Particle size distribution (percent sand, silt, and clay) was determined by the micro-pipette method (Miller and Miller, 1987). The solubility test was run in 50mL centrifuge tubes with 1g of well-mixed apatite sample and 10 mL of DI water. The samples were on the shaker for 12 days. The samples were then centrifuged and the solution was decanted. The decanted solution was analyzed for pH and then acidified and analyzed for Al, As, Ba, Cd, Ce, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, P, and Sr by ICP-AES. A detailed description of the laboratory procedure used in this study is presented in Appendix B: Work Instruction for the Laboratory Study. All phosphate materials were extracted with the USEPA standardized Toxicity Characteristic Leaching Procedure (TCLP; USEPA, 1992). The TCLP leaching solution is comprised of 0.1M glacial acetic acid and 0.0643 M NaOH, with a final pH of 4.93. Forty milliliters of leaching solution were added to 2 g of phosphate material; the mixture was agitated on a shaker for 18 hours at 25°C, and then centrifuged. After centrifugation, the supernatants were filtered through 0.22µm pore-size polycarbonate filters, acidified to 1% HNO<sub>3</sub>, and analyzed for metals by ICP-AES.

##### 3.1.2 Laboratory Measurements of Zone-of-Influence

To determine the zone-of-influence (ZOI) of sequestering materials the following experiments were conducted: phosphate sorption isotherm, ferrous iron sorption isotherm and laboratory experiment of zone-of-influence for vertical application of Fe(0) and two types of apatite.

###### 3.1.2.1 Sorption Isotherm Experiments

The objective of the phosphate and ferrous iron sorption isotherm experiments was to measure the phosphate or iron distribution coefficient,  $K_d$ , in the TNX OD sediment (from coordinate B5) to permit calculation of the effective diffusion coefficient,  $D_{eff}$ , using Fick's second law (equations 1 and 2) and equation 3 (Dragun, 1998):

$$\delta c / \delta t = (D_{eff} / R_F) (\delta^2 c / \delta x^2) \quad (1)$$

$c$  = concentration of a solute (mg/cm<sup>3</sup>)

$t$  = time (s)

$D_{eff}$  = diffusion coefficient (cm<sup>2</sup>/s),

$R_F$  = retardation factor (calculated from Equation 2)

$x$  = direction of diffusion (cm)

$$R_F = 1 + (\rho_b / \phi_e) K_d \quad (2)$$

$\rho_b$  = the porous media bulk density (mass/length<sup>3</sup>) (taken from literature for a sediment with the texture of sediment B5, loamy sand, 1.55 g/cm<sup>3</sup>) (Dragun, 1998)

$\phi_e$  = the effective porosity at saturation of media (taken from literature for a sediment with the texture of sediment B5, loamy sand, 0.47) (Hillel, 1980)

$$D_{eff} = D_o / R_F \quad (3)$$

$D_{eff}$  = diffusion coefficient,

$D_o$  = the aqueous diffusion coefficient (taken from literature),

$R_F$  = retardation factor (calculated from equation 2)

The experiment was conducted in 50ml centrifuge tubes, where 2g of well-mixed B5 sediment from the TNX OD was pre-equilibrated with non-contaminated TNX OD swamp water. Then the sediment was shaken for 4 days with a solution made of the TNX OD swamp water and an appropriate volume of PO<sub>4</sub><sup>3-</sup> (from NaH<sub>2</sub>PO<sub>4</sub>-H<sub>2</sub>O) or Fe<sup>2+</sup> (from FeCl<sub>2</sub>) solution (Tables 1B and 2B, respectively). The samples were then centrifuged and the pH, P (modified ascorbic acid method; Kuo, 1996) and Fe<sup>2+</sup>/Fe<sup>3+</sup> (1,10 – phenanthroline method; Sparks, 1996) were measured.

**Table 1.** Commercially Available Phosphate Materials Tested for Impurities

<b>Material Name/Trade Name/Location</b>	<b>Short Name*</b>	<b>Source</b>	<b>Manufacturer</b>	<b>Contact Person</b>
Natural Granulated Rock Phosphate, Montana	<b>Proc. RP-MT</b>	Processed	North Pacific AG PRODUCTS 815 NE Davis Street Portland, OR 97232	Darren McFarlane Manager dmacfarl@northpacific.com Phone: 503 872 3477
Spring Phosphate/ Powdered Rock Phosphate, Idaho	<b>Proc. RP-ID</b>	Processed	North Pacific AG PRODUCTS	
Volcanaphos- Granulated Rock Phosphate, Idaho	<b>VP Proc. RP-ID</b>	Processed	North Pacific AG PRODUCTS	
Phosphate Rock, Florida	<b>RP-FL</b>	Mined (rock phosphate)	IMC-Agrico Company 11200 Hwy 37 South Bradley, FL 33835	Bill Hall wlhall@IMCGLOBAL.COM Phone: 863 428 7161
Tennessee Brown Rock, Tennessee	<b>Brown Rock-TN</b>	Mined	Rhodia Inc. PO Box 472 Mt. Pleasant, TN 38474	Tom Mirabito Thomas.Mirabito@us.rhodia.com Phone: 931 379 3252
Washed Phosphate Ore, Tennessee	<b>Washed P Ore-TN</b>	Mined	Rhodia Inc.	
Phosphate Rock Ore, Idaho	<b>WGI RP-ID</b>	Mined	Washington Group International	Nick Lloyd Phone: 208 574 2410 ext. 33
North Carolina Apatite, NC	<b>Apatite-NC</b>	Mined	Texas Gulf Mining Aurora, NC	
Biological Apatite	<b>Biological P</b>	Biological (Ground fish bones)	PIMS-NW, Richland, WA www.pimsnw.com	Judith Wright, PIMS NW, Inc., Phone: 505 706-0211

\* The short name will be used throughout document

### ***3.1.2.2 Zone-of-Influence for Vertical Application of Fe(0) and Apatite***

The objective of this study was to determine horizontal (lateral) movement of P and Fe in sediment with vertical application of amendments. Two types of phosphate materials, mined apatite from North Carolina and biological apatite (ground fish bones, reviewed at [www.pimsnw.com](http://www.pimsnw.com)), and zero-valent iron, Fe(0) - granular Fe(0) (Peerless Supply, Columbus, OH) were tested. The sediment used in this study came from coordinate B5 in the TNX OD study site. This sediment was used because it had relatively high concentrations of constituents of interest, yet, based on analytical results, was not classified as either hazardous or radioactive. The sediment sample was collected from the top 15cm, but did not include the surface organic mat, i.e., the O sediment horizon.

Four cm of saturated sediment (B5, TNX OD) and 1.1 cm of amendment (apatite of Fe(0)) was placed in 60 mL syringes. The syringes with the saturated sediment were covered with aluminum foil to exclude light, sealed, and placed vertically on the lab bench for a period of 3 months. On August 12, 2003, the bottoms of the syringes were cut off and the samples were gently extrude out and sliced into 0.3 or 0.5cm thick slices. Each slice was collected as an individual sample. Each collected sample was digested with HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>/HCl, and the digested extracts were analyzed for total content of P, Fe and other elements by ICP-AES.

## **3.2 THE FIELD STUDY**

### **3.2.1 Zone-of-Influence for Vertical and Horizontal application Fe(0) and Apatite**

#### ***3.2.1.1 Experimental Design and Sample Collection***

The objective of the field study was to determine the zone-of-influence for amendments under field conditions in the TNX OD wetland sediments. There were two application methods (horizontal and vertical), six amendment (Control - no amendment, NC Apatite, Bio-apatite, Fe(0), NC Apatite + Fe(0), and Bio-apatite + Fe(0)) and three replicates for a total of thirty six plots (Table 1C and Figure 1). Vertical treatments were performed by augering 2cm diameter x 15cm deep holes into the ground and that backfilled with the amendment. Horizontal treatments were applied by spreading amendments over the surface of the sediment in a 30 cm by 30 cm plot. Approximately 163 g of each amendment was applied to the 30 cm by 30 cm plot; at a rate equal to 18,111 kg/ha.

Sediment samples from the horizontal and vertical treatments were collected before and 13 months after amendment application. Prior to the application of amendments, samples from the horizontal and vertical treatment areas were collected with a sediment auger into plastic sleeves (2cm diameter x 13 to 25cm). The sediment samples were collected from the center of each plot. Table 5C shows the scheme in which the samples were collected after 13 months of amendment application, labeled, and split. The sediment samples from the horizontal treatment areas were collected with a sediment sampler into plastic sleeves. Sediment samples were collected from the center of each plot (next to the hole after the first sediment sampling). Collected sediment cores were sliced into 1cm increments and each

subsample was analyzed. The sediment samples from vertical treatments were collected from the center of each plot (next to the hole after the first sediment sampling) using a sediment profiler (18cm deep x 10cm wide and 2cm thick). The collected sediment profile was divided vertically into 1cm-wide strips.

### **3.2.1.2 Methods**

A homogenized sample of all collected sediment samples from vertical, horizontal and control treatments before amendment application was sent to Savannah River Technology Center, Analytical Development Section for TCLP extraction.

The second set of sediment samples, collected almost 13 months after amendment application, was analyzed for total concentration of elements with a focus on P or Fe in extracts from a total digestion with HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>/HCl, performed on microwave system STAR 6. From the horizontal plots, each slice from two replicates of each treatment was analyzed. From the vertical plots, each slice of one replicate of each treatment was analyzed. For more details please see Appendix C, Table 6C. All extracts from the total digestion were analyzed by ICP-AES.



### 3.3 SAMPLE ANALYSIS AND QUALITY ASSURANCE

All work conducted in these studies followed Standard QA practices described in the WSRC Manual 1Q. The pH, total concentration of P and Fe and all sediment characterization measurements were made by SRTC personnel following standard procedures described in detail by Sparks (1996). Blanks and spikes were included whenever it made technical sense to do so (e.g., there is no blank control for pH measurement). Duplicates were conducted approximately every 15 analyses. The ICP-AES analyses were conducted by the Environmental Protection Department, Environmental Monitoring Section Laboratory, Westinghouse Savannah River Company. This SC DHEC-certified lab included and provided the results of laboratory blank and spike controls. Data that were outside of the certificate guidelines were not reported in this report. There were limited problems with the Th and U data; none of these compromised data are included in the report.

The lab notebook used for this study is WSRC-NB-2002-00142.

## 4 RESULTS AND DISCUSSION

### 4.1 PHOSPHATE MATERIAL CHARACTERIZATION

The nine phosphate materials (see Table 1) were evaluated for remediation of contaminated sediments. The tested materials were collected from three sources of phosphate: mined rock phosphate (Florida, Idaho, North Carolina, and Tennessee), processed rock phosphate (North Pacific AG products, Montana Natural Granulated Rock Phosphate, Spring Phosphate Powdered and Volcanaphos) and a biogenic apatite (ground fish bones – [www.pimsnw.com](http://www.pimsnw.com); PIMS-NW, Richland, WA). These phosphate materials had a pH range of 5.84 to 7.37, with the lowest pH values for processed phosphate materials (pH 5.84) and the highest for mined phosphate (pH 7.37) (Table 2). Loss-on-ignition is an approximation of organic carbon content. Organic carbon content was very high for the biological, 34.2% and only 4.3% for mined phosphate materials (Table 2). Particle size analysis showed that the texture of the phosphate materials varied substantially (Table 2). The clay fraction (<2 $\mu$ m) was the least abundant and ranged from 0.2% (Biological P) to 1.2% (Brown Rock-TN). The silt fraction, 2-50 $\mu$ m, was substantially more common than the clay fraction. The highest silt content was obtained from processed phosphate materials with a mean of 42.8%. The sand fraction, 50 $\mu$ m – 1000 $\mu$ m, was the most abundant with means of 52.4%, 60.1%, and 75.1% for processed, mined, and biological phosphate, respectively. The biological and mined phosphate materials had the highest gravel fraction (Table 2).

**Table 2.** Particle Size Distribution of Phosphate Materials

Phosphate Materials <sup>(a)</sup>	Source	pH	Organic Carbon (%, wt)	Gravel	Sand	Silt	Clay
				(%, wt)	(%, wt)	(%, wt)	(%, wt)
Proc. RP-MT	Processed	5.84 5.68	na	0.0	60.8	38.6	0.7
Proc. RP-ID				10.9	36.6	51.6	0.9
VC Proc.-ID				0.8	59.9	38.2	1.1
Avg (stdev)				3.9 6.1	52.4 13.7	42.8 7.7	0.9 0.2
PR-FL	Mined	7.37 7.74	4.3	0.0	39.0	60.4	0.7
Brown Rock-TN				8.3	65.4	25.2	1.2
Washed P Ore-TN				4.1	69.4	25.5	1.1
WGI-RP-ID				39.9	29.4	30.0	0.7
Apatite-NC				0.0	97.6	2.4	0.0
Avg (stdev)				10.5 16.8	60.1 27.0	28.7 20.7	0.7 0.5
Biological P	Biological <sup>(b)</sup>	7.10	34.2	15.5	75.1	9.1	0.2

<sup>(a)</sup> Abbreviations for minerals are defined in Table 1.

<sup>(b)</sup> Only one sample analyzed.

na – not analyzed.

High concentrations of some elements in the tested phosphate materials were expected because it is well known that these elements become concentrated into the structure of the apatite minerals. Metal concentration in apatite is the very mechanism on which this technology (in-situ immobilization) attempts to capitalize. Total concentrations of impurities in nine tested phosphate materials in comparison to the background values for surface sediment of the TNX OD (Kaplan et al., 2002) are presented in Table 3. The concentrations of several tested elements e.g., Cr, Cu, and Sr were higher in all phosphate sources relative to the background values (Table 3). The Sr concentrations reported in Table 3 are from the stable isotope, not the radioactive isotope; thus, its high concentration, e.g., 815mg/kg in the Biological-P, is not, in itself, of great concern. Also, As concentration was high for almost all tested materials; only As content in Biological P (<0.7) was lower than the background value (1.5 mg/kg).

Arsenic, Co, and Cu concentrations were among the most common impurities in the processed phosphate material (Table 4). The data presented in Table 4 show very high standard deviations, likely resulting from the varying geological origins of these materials. Therefore, the data in Table 5 are presented by the origin of phosphate. The standard deviations associated with these means do not vary nearly as much as the deviations in Table 4. The phosphate materials from Montana and Idaho generally had higher total concentrations of all tested elements because these deposits belong to the western phosphate deposition (Permian Phosphoria Formation), which is an older deposition than the Florida phosphate deposits and, therefore, they have a higher concentration of impurities. The older

phosphate deposits have a longer contact time with surrounding rock and thus have had more time to scavenge elements into their structure (Wright, 1995).

Biological P had the lowest total concentrations for almost all elements. Low concentrations in biological phosphate could be due to a short accumulation time (Wright 1995). After deposition in sediments, biogenic apatite incorporates trace elements at concentration levels that are enriched by one to many orders of magnitude over the concentration levels in the surrounding aqueous solutions (Wright 1990). This comparison of biogenic apatite *in vivo* to biogenic apatite exposed to natural water illustrates that apatite can act to greatly concentrate trace elements.

The toxicity characteristic leaching procedure (TCLP) is a regulatory test widely used to classify materials as hazardous or nonhazardous (U.S. EPA, 1990). Comparing the results of the extract analysis of phosphate materials to the regulatory levels indicated that only Cd concentrations in the processed phosphate materials exceeded (1.3 mg/kg) regulated TCLP limits (1.0 mg/kg) (Table 6). However, the difference was not statistically significant. In Table 7, the results are presented by the phosphate origin. The materials from older phosphate deposits e.g., Montana, Idaho, and Tennessee generally had higher concentrations of all tested elements in the TCLP extract; however, these concentrations were still lower than regulated TCLP limits (Table 7).

The solubility test showed that Biological P was appreciably more soluble than mined rock phosphate, i.e., Biological P had a log (K<sub>sp</sub>) of -45.2 compared to -57.0 for the mined rock phosphate (Table 8). Also the biological apatite had the highest P concentrations in the water soluble fraction, 505 mg/kg (Table 9). The total concentration of Sr in biological apatite was one of the highest; however, Sr concentration in the water soluble fraction was low, even lower than for processed phosphate materials, i.e., 2.56 mg/kg and 4.52 mg/kg, respectively, for Biological P and processed phosphate materials.

**Table 3.** Total Concentration\* (mg/kg) of Impurities in Phosphate Materials and TNX OD Background Sediment

	Background <sup>(a)</sup>	Proc.RP- MT	Proc. RP- ID	VP Proc. RP- ID	PR-FL	Brown Rock- TN	Washed P Ore- TN	WGI-PR- ID	Apatite- NC	Biological- P
As	1.5	11.1	10.2	10.0	3.7	4.8	2.3	10.5	3.8	<0.7
Ba	22	18.6	14.0	32.9	27.4	26.1	29.1	14.9	12.7	7.6
Cd	24.8	0.4	24.0	1.8	1.7	0.2	0.2	43.0	17.9	<0.03
Co	0.7	0.4	0.9	67.6	2.1	2.8	3.9	1.0	0.3	<0.07
Cr	2.8	27.6	117.0	7.5	20.1	5.4	7.2	191.6	52.5	4.6
Cu	2.2	2.7	34.3	89.4	3.4	5.0	4.7	27.5	3.9	3.3
Fe	889	932.6	3338	6147	2410.4	5788	7973	1990	1555.5	41
Mn	84	21.7	37.0	69.9	71.9	562.4	615.9	28.3	15.5	11.4
Mo	na <sup>(b)</sup>	0.9	9.7	0.1	3.4	0.8	0.5	8.0	3.8	0.8
Ni	na	7.0	67.9	17.6	11.4	10.0	12.8	76.7	10.8	<0.7
Pb	12.2	11.5	5.1	21.0	6.3	4.2	5.7	2.9	3.1	1.3
Sr	na	95.9	175.0	442.5	285.7	146.6	187.4	150.6	544.8	815.0

\* Each phosphate sample was analyzed in two replicates

(a) Kaplan et al. (2002), sediment background values are for surface sediment collected just north of the operable unit.

(b) Not analyzed

**Table 4.** Concentration (mg/kg) of Impurities in Tested Phosphate Sources

	Processed <sup>(a)</sup>		Mined		Biological	
	Avg	Stdev	Avg	Stdev	Avg	Stdev
As	10.4	1	5.1	0.3	<0.7	NA
Ba	21.8	9	22.0	7.0	7.6	0.1
Cd	8.7	12	12.6	19.0	<0.03	NA
Co	23.0	35	2.0	1.0	<0.07	NA
Cr	50.7	54	55.4	80.0	4.6	0.0
Cu	42.1	39	8.9	10.0	3.3	1.5
Fe	3472.7	2346	3943.0	2672.0	41.0	0.2
Mn	42.9	22	258.8	290.0	11.4	0.2
Mo	3.6	5	3.3	3.0	0.8	0.1
Ni	30.8	29	24.3	30.0	<0.7	NA
Pb	12.5	7	4.4	2.0	1.3	0.1
Sr	237.8	170	263.0	132.0	815.0	136.0

<sup>(a)</sup> The number of observations for each mean varies; processed=6, mined=12, biological=2  
 NA – not applicable

**Table 5.** Total Concentration\* (mg/kg) of Impurities in Tested Phosphate Origin

	Montana		Idaho <sup>(a)</sup>		Tennessee <sup>(b)</sup>		North Carolina		Florida		Biological	
	Avg	Stdev	Avg	Stdev	Avg	Stdev	Avg	Stdev	Avg	Stdev	Avg	Stdev
As	11.1	0.7	10.3	0.6	3.6	1.7	3.8	NA	3.7	0.6	<0.7	NA
Ba	18.6	0.0	20.6	9.7	27.6	2.7	12.7	NA	27.4	0.2	7.6	0.1
Cd	0.4	0.0	22.9	18.8	0.2	0.0	17.9	NA	1.7	0.1	<0.03	NA
Co	0.4	0.0	23.2	34.5	3.4	0.9	0.3	NA	2.1	0.2	<0.07	NA
Cr	27.6	3.4	105.4	86.5	6.3	1.1	52.5	NA	20.1	0.1	4.6	0.0
Cu	2.7	1.7	50.4	30.5	4.9	0.7	3.9	NA	3.4	0.8	3.3	1.5
Fe	932.6	87.7	3824.9	1918.8	6880.4	1298.5	1555.5	NA	2410.4	109.9	40.9	0.2
Mn	21.7	4.0	45.1	20.5	589.2	56.6	15.5	NA	71.9	0.8	11.4	0.2
Mo	0.9	0.1	5.9	4.7	0.7	0.3	3.8	NA	3.4	0.3	0.8	0.1
Ni	7.0	0.8	54.1	29.7	11.4	1.8	10.8	NA	11.4	0.4	<0.7	NA
Pb	11.5	1.8	9.7	8.9	5.0	1.1	3.1	NA	6.3	0.3	1.3	0.1

\* Each material was analyzed in two replicates

<sup>(a)</sup> Idaho = 3 materials: Proc. RP-ID, VP Proc. RP-ID, and WGI RP-ID

<sup>(b)</sup> Tennessee = Brown Rock-TN and Washed P Ore-TN

NA – not applicable

**Table 6.** Concentration of Elements\* (mg/kg) in TCLP Extract of Phosphate Sources

Elements	Regulatory Level <sup>(a)</sup> [mg/L]	Processed <sup>(b)</sup>		Mined		Biological	
		Avg	Stdev	Avg	Stdev	Avg	Stdev
As	5.0	1.1	0.9	1.0	0.7	0.8	0.0
Ba	100.0	2.1	1.7	1.0	0.5	0.3	0.0
Ca	NL	13333.4	7692.1	3708.6	2047.1	7620.0	145.2
Cd	1.0	1.3	1.0	0.9	2.0	<0.003	0.0
Co	NL	19.5	33.5	0.1	0.2	<0.02	0.0
Cr	5.0	0.5	0.5	0.1	0.0	0.1	0.0
Cu	NL	13.6	21.6	0.1	0.0	0.2	0.1
Fe	NL	58.0	94.5	<1.6	0.0	<1.6	0.0
Mg	NL	689.7	70.6	326.6	279.2	1592.5	48.8
Mn	NL	50.4	61.5	15.1	18.6	0.1	0.0
Mo	NL	0.5	0.4	9.4	20.7	0.1	0.0
Ni	70	8.1	11.2	2.1	3.2	<0.16	0.0
Pb	5.0	0.2	0.1	<0.12	0.0	<0.12	0.0
P	NL	1072.9	1752.5	168.0	139.4	3234.9	51.8
Sr	NL	22.3	13.5	21.7	31.8	63.2	1.5

\* Each material was tested in two replicates.

<sup>(a)</sup> Maximum concentration of contaminants for toxicity characteristics (40 CFR 261.24, U.S. EPA, 1999)

<sup>(b)</sup> The number of observations for each mean varies; processed=6, mined=12, biological=2  
 NL – no RCRA limit

**Table 7.** Concentration of Elements\* (mg/kg) in TCLP Extract of Phosphate Origin

Elements	Regulatory Level [mg/L]	Montana		Idaho <sup>(a)</sup>		Tennessee <sup>(b)</sup>		North Carolina		Florida		Biological	
		Avg	Stdev	Avg	Stdev	Avg	Stdev	Avg	Stdev	Avg	Stdev	Avg	Stdev
As	5.0	1.20	0.19	1.21	0.96	1.60	0.00	<0.2	0.00	0.25	0.08	0.84	0.03
Ba	100.0	3.97	0.19	1.33	0.7	0.95	0.55	0.61	0.02	0.65	0.02	0.33	0.01
Ca	NL	21041	548	7166	5538	2728	1608	7004	272	3544	431	7620	145
Cd	1.0	0.15	0.01	2.73	1.6	<0.003	0.00	<0.003	0.00	0.02	0.00	<0.003	0.00
Co	NL	0.36	0.01	19.40	33.6	<0.02	0.01	<0.02	0.00	0.51	0.06	<0.02	0.00
Cr	5.0	1.04	0.05	0.22	0.2	<0.04	0.00	0.05	0.00	0.05	0.00	0.13	0.00
Cu	NL	2.23	0.15	12.92	22.2	0.14	0.03	0.08	0.00	0.13	0.00	0.17	0.05
Fe	NL	167.11	7.73	2.83	2.1	<1.6	0.00	<1.6	0.00	0.81	0.74	<1.6	0.00
Mg	NL	655.88	3.07	679.40	79.6	51.18	70.12	321.75	19.44	583.79	68.01	1592.51	48.80
Mn	NL	26.85	0.78	41.86	67.8	34.08	13.10	1.17	0.01	4.68	0.43	0.12	0.00
Mo	NL	0.59	0.04	0.35	0.5	23.26	32.81	0.05	0.00	0.12	0.01	0.06	0.01
Ni	70	0.82	0.08	10.36	9.6	0.18	0.03	0.71	0.06	1.81	0.23	<0.16	0.00
Pb	5.0	0.32	0.05	0.15	0.1	<0.12	0.00	<0.12	0.00	<0.12	0.00	<0.12	0.00
P	NL	90.32	1.03	1081.56	1745.3	100.81	56.55	110.30	5.81	411.83	29.04	3234.94	51.79
Sr	NL	31.11	0.16	14.76	12.4	5.28	3.44	78.32	3.45	11.22	1.36	63.15	1.48

\* Each material was tested in two replicates.

<sup>(a)</sup> Idaho = 3 materials: Proc. RP-ID, VP Proc. RP-ID, & WGI RP-ID; 2 replicates of each material

<sup>(b)</sup> Tennessee = Brown Rock-TN and Washed P Ore-TN; 2 replicates of each material

NL – no RCRA limit

**Table 8.** Solubility of Phosphate Materials in Comparison with Some Phosphate Mineral Phases; the Solubility was Calculated by Following Davies Equation (Sposito, 1986)

Phosphate Materials	Avg pH	Avg log(Ksp)	Mineral Phase	Log (Ksp)
Processed	6.67	-48.0	Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (OH,Cl)	-76.5
Mined	7.40	-57.0	Sr <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (OH)	-51.3
Biological	7.10	-45.2	Zn <sub>3</sub> (PO <sub>4</sub> ) <sub>3</sub>	-35.3
			Cd <sub>3</sub> (PO <sub>4</sub> ) <sub>3</sub>	-32.6
			Pu(PO <sub>4</sub> )	-24.4
			Quartz (SiO <sub>2</sub> )	-4
Davies Eq.: log(Ksp) = 10log(Ca) + 6log(PO <sub>4</sub> <sup>3-</sup> ) + 2log(OH)				

**Table 9.** Concentration of Elements\* (mg/kg) in Water Soluble Fraction of Phosphate Materials

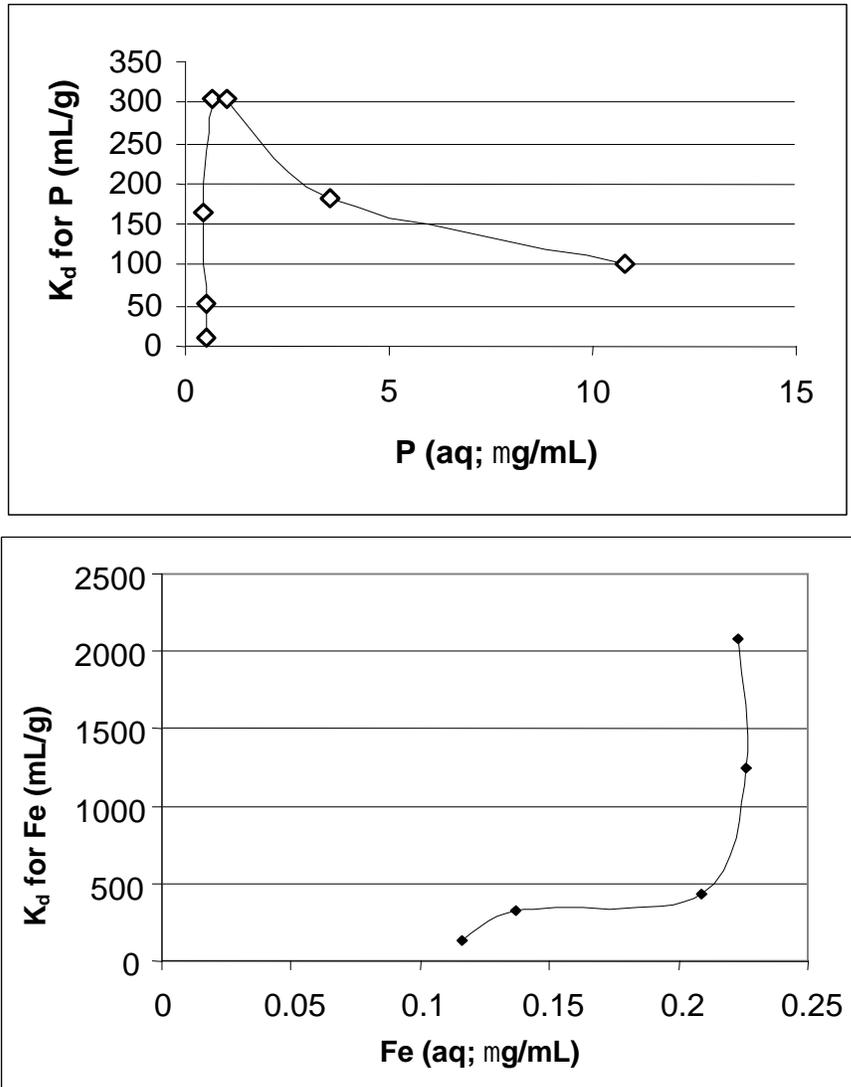
Elements (mg/kg)	Processed <sup>(a)</sup>		Mined		Biological	
	Avg	Stdev	Avg	Stdev	Avg	Stdev
As	1.02	0.98	0.06	0.04	0.32	0.01
Ba	0.34	0.27	0.10	0.12	0.01	0.00
Ca	1593.18	1111.11	185.31	137.15	278.70	38.76
Cd	0.25	0.20	0.08	0.17	0.00	0.00
Co	9.50	14.58	0.01	0.01	0.00	0.00
Cr	1.03	1.05	0.55	1.18	0.04	0.02
Cu	6.41	9.63	0.06	0.11	0.02	0.00
Fe	57.99	72.17	6.67	8.09	0.38	0.04
Mg	196.19	136.71	29.88	32.38	200.52	14.34
Mn	16.13	24.11	0.53	0.73	0.01	0.00
Mo	0.19	0.14	0.15	0.18	0.04	0.01
Ni	3.78	4.60	0.45	0.86	0.05	0.01
Pb	0.10	0.05	0.03	0.01	0.03	0.00
Sr	4.52	3.54	0.93	1.37	2.56	0.35
P	307.31	458.27	20.20	26.41	504.81	77.09

\* Each material was tested in three replicates.

<sup>(a)</sup> The number of observations for each mean varies; processed=9, mined=18, biological=3

**4.2 EFFECTIVE DIFFUSION COEFFICIENTS CALCULATED FROM  $K_d$  VALUES**

The objective of the phosphate and ferrous iron sorption isotherm experiments was to measure the phosphate or iron distribution coefficient,  $K_d$ , in the TNX OD sediment (B5) (Figure 2) to permit calculation of an effective diffusion coefficient,  $D_{eff}$ , using equations 1, 2, and 3. These values are presented in Table 10. The  $K_d$  based  $D_{eff}$  values were in the order of  $10^{-8} \text{ cm}^2/\text{s}$  and provide a theoretical estimate based on a number of chemical assumptions (no precipitation, reversible adsorption/desorption, linear isotherm behavior, etc...) (Table 10).



**Figure 2.** The Distribution Coefficients ( $K_d$ ) for P and Fe for the Sediment (B5) from the TNX OD

**Table 10.** Effective Diffusion Coefficients ( $\text{cm}^2/\text{s}$ ) Calculated from Field Data, Laboratory Data, and  $K_d$  Values

	Field <sup>(a)</sup>	Laboratory <sup>(a)</sup>	Calculated from $K_d$ <sup>(b)</sup>
Biological Apatite	NA	1.76e-6	1.98e-8
NC Apatite	6.71e-6	1.97e-6	1.98e-8
Fe(0)	1.77e-6	2.91e-6	1.21e-8
<sup>(a)</sup> Calculated from equation 1 and 2.			
<sup>(b)</sup> Calculated from equations 3: assuming Fe $K_d = 200 \text{ mL/g}$ and P $K_d = 125 \text{ mL/g}$ from Figure 2, porosity = 0.4, particle density = $1.65 \text{ g/cm}^3$ , Fe & P diffusion in water = $1\text{e-}5 \text{ cm}^2/\text{s}$ from Dragun, 1998 and Hillel, 1980.			
NA – not analyzed			

Figure 2 presents  $K_d$  values as a function of aqueous P and Fe concentrations. These types of graphs are referred to as sorption isotherms and can provide indirect evidence regarding how a solute, in this case P or Fe, sorb to the solid phase. At low aqueous P concentrations, there is a steep increase in  $K_d$  values, followed by a gradual decline. This is a common isotherm pattern for solutes that sorb strongly to a sediment, but once the “high energy” sorption sites are filled, the proportion of solid to aqueous phase P concentrations gradually decrease generally in a linear manner with respect to aqueous P concentrations.

The sorption isotherm for Fe was quite different from that for P (Figure 2). At low concentrations, the Fe gradually sorbed onto the sediment, but after a critical point,  $\sim 0.21 \mu\text{g/mL}$ , the  $K_d$  value increases sharply. This isotherm pattern is a classic example of a moderately strong sorbing solute precipitating out of solution once solubility is exceeded.

This type of data underscores the importance of using isotherm data, as compared to single sorption values, such as a  $K_d$  value, to represent solute geochemical behavior in sediments. However, in the case of Fe, solubility maintains the aqueous Fe concentrations to  $<0.2 \mu\text{g/mL}$ , thereby greatly limiting the range of possible  $K_d$  values. Thus, a combination of both solubility controls and  $K_d$  values may be best for describing Fe geochemistry in this system. In the case of P, solubility does not appear to have been exceeded and the apparent  $K_d$  values varied greatly over the range of aqueous P concentrations evaluated. Sediment porewater P concentrations at TNX OD are  $<1 \text{ mg/L}$ , and as such, are expected to sorb to the sediment in greatly varying degrees, depending on slight changes in the aqueous concentrations.

### 4.3 ZONE-OF-INFLUENCE (ZOI) OF AMENDMENTS UNDER LABORATORY CONDITIONS

The laboratory experiment was conducted under controlled conditions in a 60mL syringe at 21°C. As such, they isolate the diffusion process from other water transport processes that may occur under natural field conditions, such as advection, colloidal transport, and macro-pore flow. In the laboratory study, diffusion of P and Fe was determined by the measurement of these element concentrations in sediment B5, which was in contact with North Carolina Apatite, biological P or zero-valent iron, [Fe(0)] for three months. The data for the biological P and North Carolina apatite are presented in Figure 3. These concentrations were then used to calculate effective diffusion coefficients ( $D_{\text{eff}}$ ) (Table 10). The estimated Fe and P  $D_{\text{eff}}$  values were similar, in the order of  $10^{-6}$  cm<sup>2</sup>/s (Table 10).

Diffusion is a spontaneous process that results in the movement of a solute. Diffusion is caused by the random thermal motion of a solute in solution and is driven by concentration gradients. Solutes move from high concentration areas to low concentration areas. To provide a measure of lateral movement of the P and Fe in the vertical treatments, laboratory data were collected and applied to diffusion equations (Fick's second law and equation 3) to provide effective diffusion coefficients.

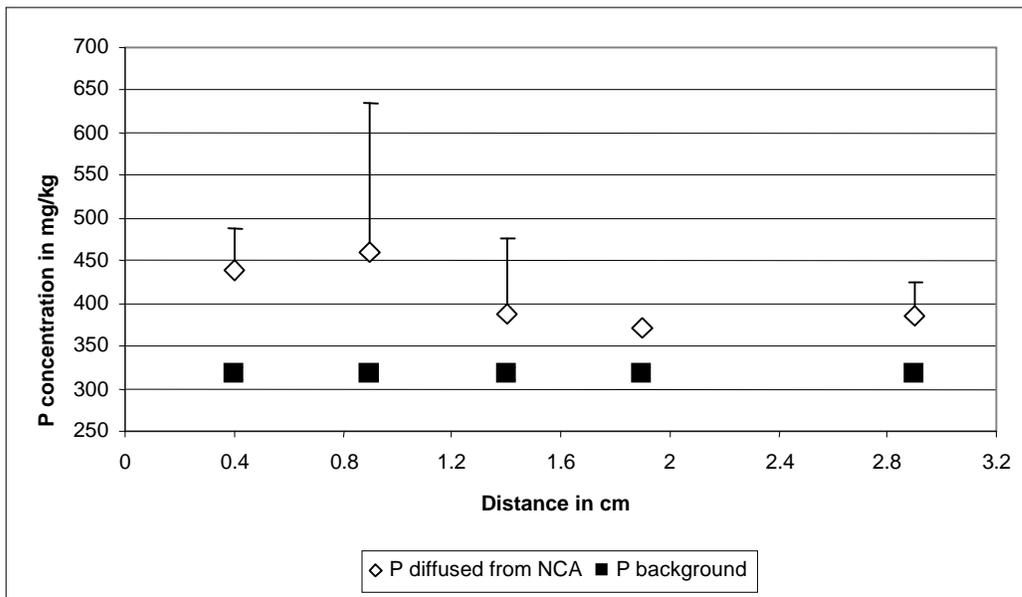
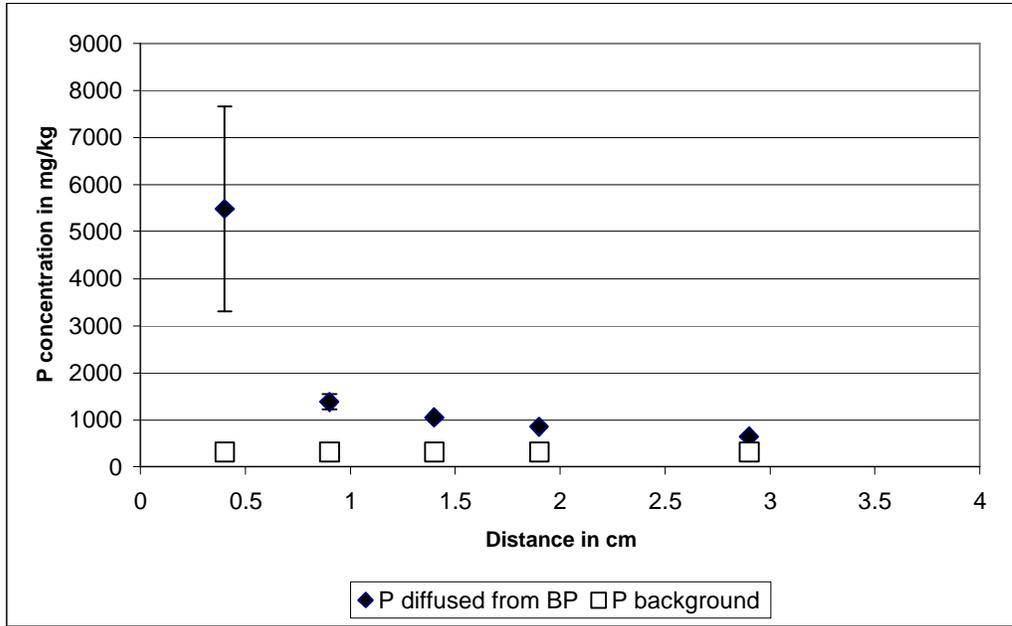
The background P concentration in B5 sediment was 318 mg/kg (Table 11). In the treatment with biological apatite, the P concentration was the highest in the first slice of the sediment (a distance from apatite of 0 to 0.4 cm), 5484 mg/kg (Table 11). The P concentration in the second slice was drastically lower than in the first slice but still higher than the P background concentration (Figure 3). In remaining three further slices, i.e., the distance from 0.9 cm to 2.9 cm, P concentrations remained higher than the P background concentration for this sediment. In the treatment with NC apatite, the P concentration was the highest in the first two slices of the sediment; however, it was considerably lower than in the treatment with biological apatite (Figure 4 and Table 11). In the treatments with metallic iron, in a period of three months, Fe traveled the distance of less than 1.0 cm, and the highest concentration of Fe was observed in the first slice, 15095 mg/kg (Figure 4 and Table 11).

**Table 11.** Diffusion of P or Fe in Treatments with Phosphate Source or Fe(0); Laboratory Experiment, Average Values Based on Two Replicates

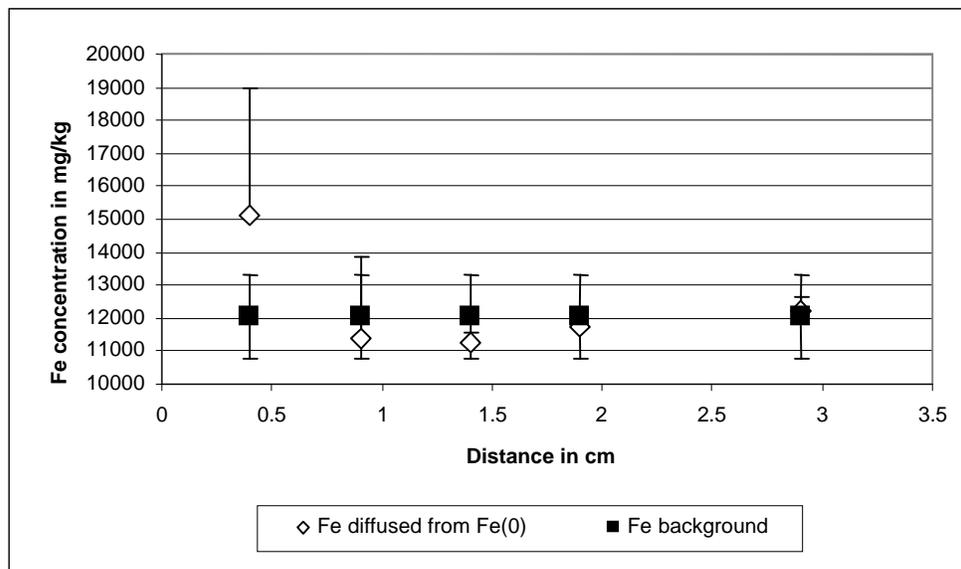
Diffusion of P (P concentration in mg/kg)					
Treatments	Distance (cm) from P source				
	0.5	1	1.5	2	2.5
Background (B5) avg	318	318	318	318	318
Background (B5) stdev	7.6	7.6	7.6	7.6	7.6
Biological-P avg	5484	1386	1054	849	640
Biological-P stdev	2183	167	30	30	11
Ncapatite avg	440	460	388	372	386
NCapatite stdev	47	174	88	2	40

Diffusion of Fe (Fe concentration in mg/kg)					
Treatments	Distance (cm) from Fe source				
	0.5	1	1.5	2	2.5
Background (B5) avg	12052	12052	12052	12052	12052
Background (B5) stdev	1248	1248	1248	1248	1248
Fe(0) avg	15095	11402	11241.5	11770.5	12229
Fe(0) stdev	3855	2427	313	455	434



**Figure 3.** Profile of P Diffusion in the B5 Sediment from the TNX OD after 3 Months of Contact with Biological P (BP) and North Carolina (NCA): Laboratory Study



**Figure 4.** Profile of Fe Diffusion in the B5 Sediment from the TNX OD after 3 Months of Contact with Fe(0): Laboratory Study

#### 4.4 ZONE-OF-INFLUENCE (ZOI) OF AMENDMENTS UNDER FIELD CONDITIONS

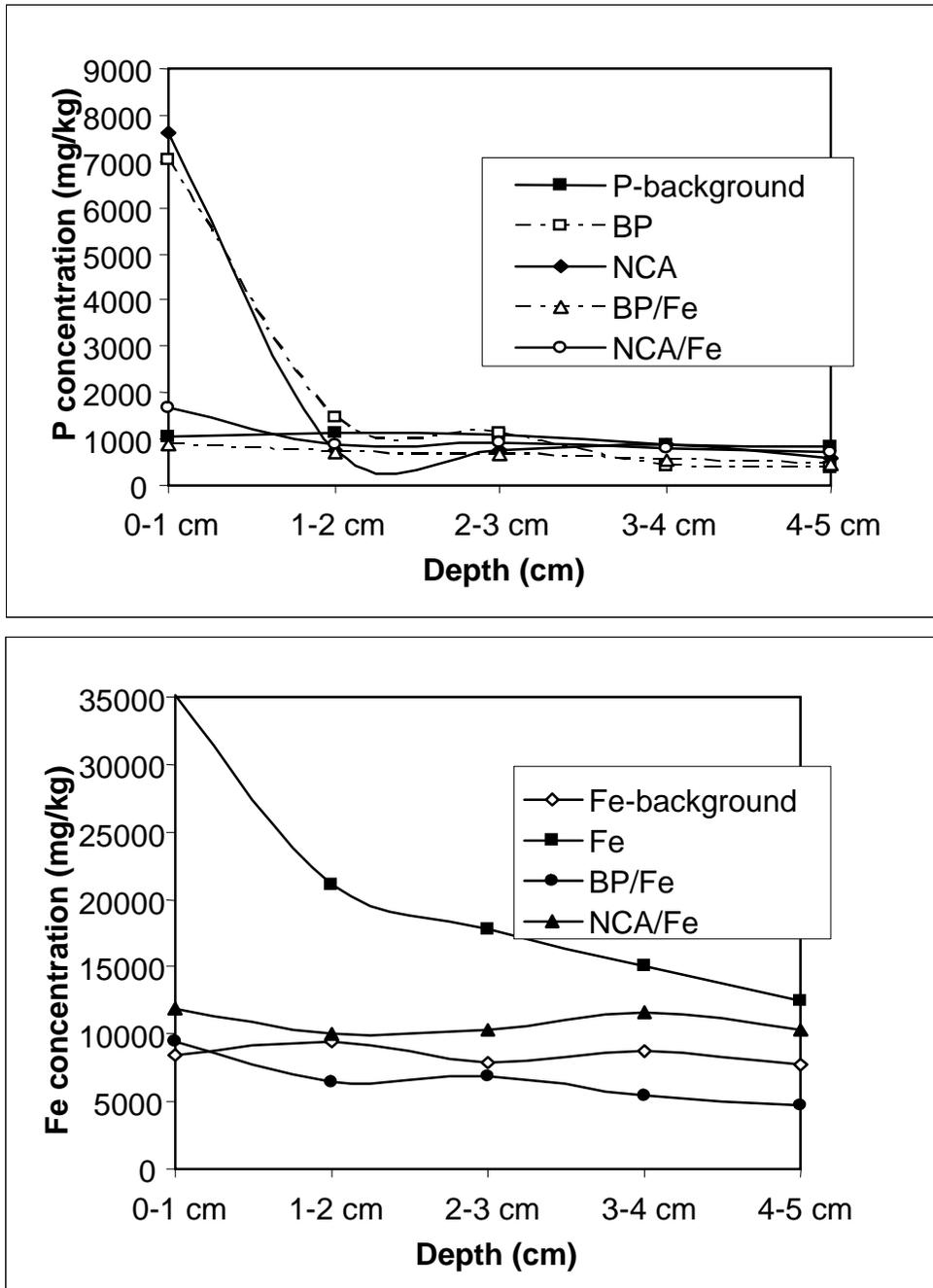
In the horizontal treatments five amendments (North Carolina Apatite, biological apatite, Fe (0), and F(0) mixed with North Carolina Apatite and Fe(0) mixed with biological apatite) were spread on the surface of the sediment. For the treatments with P source, i.e., apatite minerals or apatite mixed with Fe(0), the transport of P as a function of depth was evaluated. The transport of P in these treatments occurred very likely by saturated flow, involving diffusion and advection. The background average concentration of P in the sediment top layer (zero distance from  $\text{PO}_4^{3-}$  source) was 1057 mg/kg and it decreased to less than 900 mg/kg in the last two bottom layers tested, i.e., depth from 3 to 5 cm (Figure 5 and Table 8C). Addition of North Carolina Apatite and biological apatite significantly increased the P concentrations in the two first layers (i.e., depth from 0 to 2 cm) up to 7030 and 7634 mg/kg, respectively, in plots with North Carolina Apatite and biological apatite (Figure 5). In depths from 2 cm to 5 cm, P concentrations in plots with both types of apatite remained similar to the background P concentrations.

Concurrent applications of apatite (North Carolina or biological) and Fe(0) did not induce P or Fe transport through the sediment profile. The P and Fe concentration distribution in the sediment in these treatments was similar to the P and Fe distribution in the background sediment (Figure 5). Phosphate has been reported to be chemically associated with Fe in soils or sediments (Wang et al., 1991). Very likely in the presence of high content of  $\text{PO}_4^{3-}$  and Fe, under reducing conditions ferrous phosphates, e.g., vivianite [ $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ] precipitated. In the treatment where only Fe(0) was added, Fe traveled to the depth of 5 cm; however, the highest Fe concentrations were observed in the first three layers, i.e., to the depth of 3 cm (Figure 5).

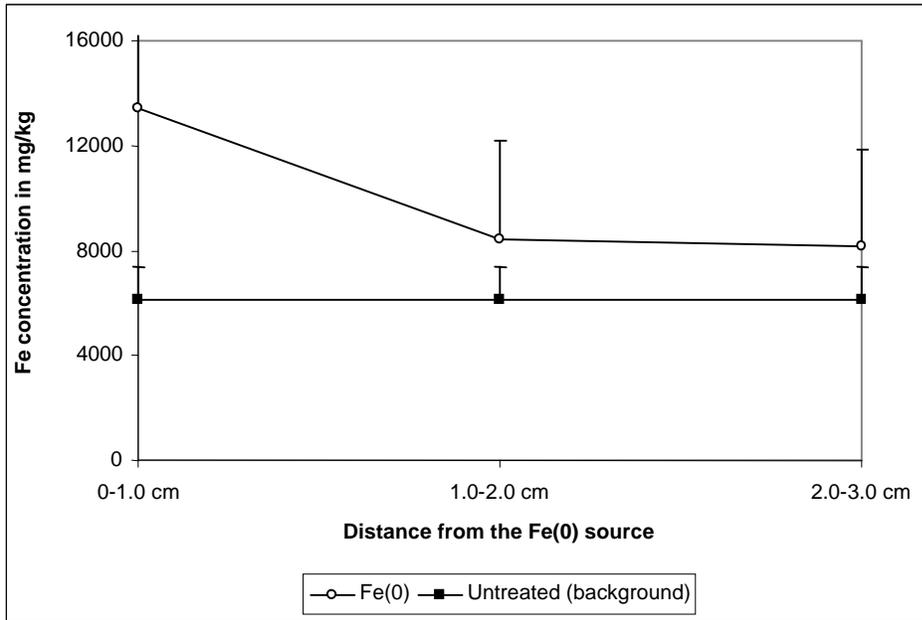
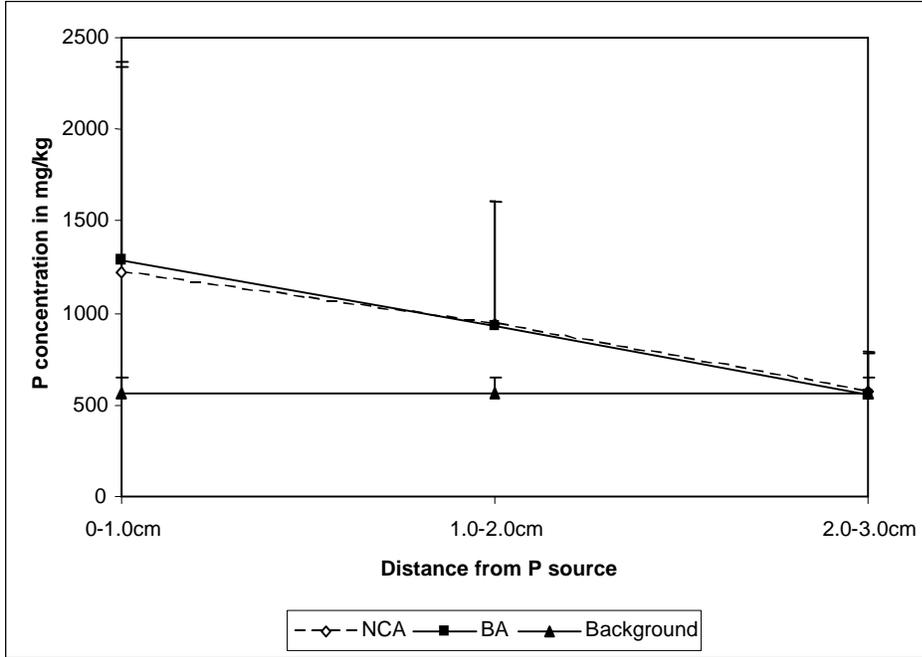
In the vertical treatments (lateral distance) where the amendments were added to a hole 15 cm deep, the transport of elements of interest, i.e., P and Fe, was based only on saturated diffusion. The analyzed distance from the source of P or Fe was 3 cm. The distance of 3 cm was divided into three strips (1 cm wide) and data for each strip are presented in Figure 6.

The diffusion of P from both sources of P, i.e., North Carolina and biological apatite, were almost identical (Figure 6). Phosphorous in these two treatments traveled 2 or 2.5 cm. The background Fe concentration in the tested site sediment was 6101 mg/kg, applied Fe(0) increased Fe concentrations in all tested strips of the sediment and data showed that Fe diffused though the longer distance than P (Figure 6).

Effective diffusion coefficients based on the field data were in the order of  $10^{-6}$  cm<sup>2</sup>/s, values very similar to those derived from the laboratory study (Table 10). The two order of magnitude greater rate than the theoretical value based on  $K_d$  values likely indicates that the underlying assumptions based on the theoretical values are inappropriate.



**Figure 5.** Transport of P and Fe in the Horizontal Treatments; the Total Evaluated Depth from the Element Source was 5 cm



**Figure 6.** Transport of P and Fe in the Vertical Treatments; the Evaluated Distance for Element was 3 cm

#### 4.5 PHOSPHORUS AND IRON DIFFUSION MODELING

Sediment P and Fe concentration data were obtained from the laboratory and field study for calculations of P and Fe(0) diffusion. Metallic iron, biological P and North Carolina apatite were used in those tests. Utilizing PORFLOW™ software, the diffusion coefficients for P and F(0) were estimated based on the test data.

PORFLOW™ is developed and marketed by Analytic & Computational Research, Inc. to solve problems involving transient and steady-state fluid flow, heat and mass transport in multi-phase, variably saturated, porous or fractured media with dynamic phase change. The porous/fractured media may be anisotropic, arbitrary heterogeneous sources (injection or pumping wells) may be present and, chemical reactions or radioactive decay may take place. PORFLOW™ has been widely used in the DOE complex to address major issues related to groundwater and nuclear waste management. PC-based PORFLOW™ Version 4.0 (dated 14 September 2000) was used in this work.

To calculate P and Fe(0) diffusion, PORFLOW™ models were set up to reflect the initial test conditions. The models were run to simulate both the laboratory and field tests. Note that the concentration data were obtained from the 91-day (~3 months) laboratory experiments and from the 395-day (13 months) field study. Effective diffusion coefficients are optimized so that the modeling results would closely agree with the test data.

Table 12 lists the optimal effective diffusion coefficients of Fe(0), biological P, and NC apatite for the laboratory and field studies. Overall, except for biological P, the diffusion coefficients for both studies are in agreement within one order of magnitude. The biological P data strongly suggests that precipitation occurred, a process that was not simulated in our PORFLOW™ models.

Using the optimal effective diffusion coefficients obtained from the field study, the radius distance that Fe and P diffused away from an infinite source term was calculated as a function of time. The calculated aqueous P or Fe concentration used to set the outer limit of diffusion was  $1E^{-7}$  M above background levels (note: the computer calculates concentrations  $<1E^{-21}$  M, such concentrations would have no impact on sequestration, the phenomena of interest). For biological and NC apatite, an effective diffusion coefficient of  $1.865E^{-6}$  cm<sup>2</sup>/s (i.e., average of the two estimated diffusion coefficients) was used. The results are summarized in Table 12. Similar distance calculations were not conducted with the laboratory-derived diffusion coefficients because of their similarity with the field-derived values.

**Table 12.** Calculated P and Fe Effective Diffusion Coefficients (D<sub>eff</sub>) Based on Laboratory and Field study. Calculated Radius of Sediment Amendment Zone-of-Influence Based on Field Study

Amendment	Laboratory		Field			
	D <sub>eff</sub> (cm <sup>2</sup> /s)	D <sub>eff</sub> (cm <sup>2</sup> /s)	Radius Distance P or Fe Travels in T-Area Sediment <sup>†</sup> (cm)			
			13 months	5 yr	7 yr	10 yr
Fe(0)	1.77E <sup>-6</sup>	2.9E <sup>-6</sup>	2.1	4.5	5.2	6.3
Biological P	3.0E <sup>-7</sup>	1.76E <sup>-6</sup>	2.3	4.9	5.8	6.9
NC Apatite	6.7E <sup>-6</sup>	1.97E <sup>-6</sup>	1.8	3.9	4.6	5.5

<sup>†</sup>: Determined at concentration of 1E<sup>-7</sup> mol/L. For Biological P and NC Apatite, average D<sub>eff</sub> of 1.865E<sup>-6</sup> cm<sup>2</sup>/s was used.

## 5 CONCLUSIONS

Nine commercially available phosphate minerals were evaluated for solubility, concentration of trace metals, and leachability of trace metals. Processed and mined rock phosphate contain high total concentrations of As, Co, Cr, Cu, and Sr, however, they did not exceed the RCRA TCLP limits. The use of stronger extractants indicated that these elements were very strongly bound by most apatite material; therefore, if they were applied to contaminated sediment at a rate sufficient for remediation, they would not pose an environmental risk. The biogenic apatite (fish bone) contained significantly lower metal impurities than processed and mined rock phosphate and was appreciably more soluble, i.e., it had a  $\log K_{sp}$  of -45.2 compared to -57.0 for the mined rock phosphate samples.

The ZOI of surface applied amendments (horizontally applied), and amendments backfilled into holes (vertically applied) were evaluated under field conditions. Additionally, vertical application of ZOI was tested in the lab. For the surface applied amendments in the 13-month field study, P from the biological apatite and from the mined apatite moved ~3 cm; and Fe from the Fe(0) treatment moved ~5 cm. Retardation factors were calculated and used to estimate the zone-of-influence at various intervals. To provide a measure of lateral movement of the P and Fe in the vertical treatments, field and laboratory data were collected and applied to diffusion equations (Fick's second law) to provide effective diffusion coefficients. Both sets of data were reasonably consistent, indicating that P from the biological and mined apatite and Fe from Fe(0) would be expected to diffuse more than 5 cm after 10 years. Both downward and lateral movement of P and Fe were greatly reduced when Fe(0) and apatite were applied concurrently. Based on thermodynamic calculations, an iron phosphate phase precipitated from solution, reducing the migration of each mineral, thereby greatly reducing the zone-of-influence.

In summary, there are several sources of phosphate that may be safely and effectively applied to the site. By mixing biogenic with mined phosphate, it will be possible to obtain a wide range of phosphate solubility, permitting the rapid immobilization of contaminants, while at the same time providing a slow release of phosphate for continued sediment treatment. Both materials are inexpensive and locally available: biological phosphate from Florida (perhaps South Carolina) and mined phosphate from North Carolina. The zone-of-influence for these amendments will increase relatively slowly. It will not be possible to apply Fe(0) along with apatite to the site and create a large zone-of-influence because an iron-phosphate phase precipitates, greatly reducing the mobility, and therefore the zone-of-influence of iron and phosphate. If both amendments are deemed necessary, it would be best to apply them at different times.

## 6 ACKNOWLEDGEMENTS

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## 7 REFERENCES

- Dragun, J. 1998. *The Sediment Chemistry of Hazardous Materials*, 2<sup>nd</sup> edition. Amherst Scientific Publisher, Amherst, MA.
- Eary, L. E., and D. Rai. 1987. Kinetics of Chromium(III) Oxidation to Chromium(VI) by Reaction with Manganese Dioxide. 21:1187-1193.
- Hillel, D. 1980. *Fundamentals of Sediment Physics*. Academic Press. New York.
- Kaplan, D., A.S. Knox, and C. Coffey. 2002. Reduction of Contaminant Mobility at the TNX OD Outfall Delta Through the use of Apatite and Zero-Valent Iron as Sediment Amendments (U). WSRC-TR-2002-00370, Rev. 0 Westinghouse Savannah River Company, Aiken, SC.
- Knox, A.S., D.I. Kaplan, D.C. Adriano, T.G. Hinton, and M.D. Wilson. 2003. Apatite and Phillipsite as Sequestering Agents for Metals and Radionuclides. *J. Environ. Qual.* 32: 515-525.
- Knudsen, A. C., and M. E. Gunter. 2002. Sedimentary Phosphorites-An Example: Phosphoria Formation, Southeastern Idaho, USA. In: M.J. Kohn, J. Rakovan and J.M. Hughes (Eds), *Phosphates – Geochemical, Geobiological, and Materials Importance*, Reviews in mineralogy and geochemistry, Vol. 48 Mineralogical Society of America, Washington, DC.
- Kuo, S. 1996. Phosphorus. In: D. L. Sparks (ed), *Methods of Sediment Analysis, Part 3 – Chemical Methods*. pp. 869 – 919. Sediment Science Society of America, Madison, WI.
- Ma, Q.Y., T.J. Logan, and S.J. Traina. 1995. Lead immobilization from aqueous solutions and contaminated sediments using phosphate rocks. *Environ. Sci. Technol.* 29: 1118-1126.
- Melita, N. M. Conklin, and J. Ferrell. Electrochemical Study of Arsenate and Water Reduction on Iron Media Used for Arsenic Removal from Potable Water. *Environ. Sci. Technol.* 36(14):3188-3193.
- Miller, W. P. and D. M. Miller. 1987. “A Micro-Pipette Method for Sediment Mechanical Analysis.” *Communications In Sediment Sci., Plant Anal.* 18(1) 1-15.
- Runchal, A. 2000. PORFLOW: A Model for Fluid Flow, Heat, and Mass Transport in Multifluid, Multiphase, Fractured, or Porous Media. User's manual - Version 4.0. Analytical and Computational Research, Inc (ACRI), Bel Air, CA.
- Ryan, J.A., P. Zhang, D. Hesterberg, L. Chou, and D.E. Sayers. 2001. Formation of chloropyromorphite in a lead-contaminated sediment amended with hydroxyapatite. *Environ. Sci. Technol.* 35:3798-3803.
- Sass, B. M., and D. Rai. 1987. Solubility of Amorphous Chromium(III)-Iron(III) Hydroxide Solid Solutions. *Inorganic Chemistry.* 26:2228-2232.

Seaman, J.C., T. Meehan, and P.M. Bertsch. 2001. Immobilization of cesium-137 and uranium in contaminated sediments using sediment amendments. *J. Environ. Qual.* 30:1206-1213.

Sparks, D.O. 1996. *Methods of Sediment Analysis, Part 3 – Chemical Methods*. Sediment Science Society of America, Inc., Madison, Wisconsin.

Suzuki, T., T. Hatsushika, and M. Miyake. 1982. Synthetic Hydroxyapatite as inorganic cations exchangers. *J. Chem. Soc., Faraday Trans. I.* 78:3605-3611.

Suzuki, T., T. Hatsushika, and Y. Hayakawa. 1981. Synthetic Hydroxyapatite employed as inorganic cation-exchangers. *J. Chem. Soc., Faraday Trans. I.* 77:1059-1062.

Thomas, G. W. 1996. Sediment pH and Sediment Acidity. In: D. H. Sparks (ed.) *Methods of Sediment Analysis, Part 3, Chemical Methods*, Sediment Science Society of America and American Society of Agronomy, Madison, Wisconsin.

U.S. EPA. 1992. Toxicity Characteristic Leaching procedure. Method 1311, Rev.0. In SW-846: Test methods for evaluating solid waste, physical/chemical methods. Office of Solid Waste, Washington, DC.

U.S. EPA, 1999. Identification and Listing of Hazardous Waste, Toxicity Characteristics. 40 CFR 261.24, Federal Register, vol. 18, no. 261, pp. 55-56, July 1, 1999.

WSRC (Westinghouse Savannah River Company). 1990. RFI/RI with BRA for the TNX OD Outfall Delta, Lower Discharge Gully and swamp operable Unit. WSRC\_RP-98-4158, Rev. 0. Westinghouse Savannah River Company, Aiken, SC.

Winer, B. J. 1971. *Statistical Principles in Experimental Design*. McGraw-Hill, Inc.

Wright, J. 1990. Conodont Apatite: Structure and Geochemistry. In: J. Carter (Ed.), *Metazoan Biomineralization: Patterns, Processes and Evolutionary Trends*. Pp. 445-459, Van Nostrand Reinhold, New York.

Wright, J. V., L. M. Peurrung, T. E. Moody, J. L. Conca, X. Chen, P. P. Didzerekis, and E. Wyse. 1995. *In Situ Immobilization of Heavy Metals: Apatite Mineral Formations*. Technical Report to the Strategic Environmental Research and Development Program, Department of Defense, Pacific Northwest National Laboratory, Richland, WA p. 154.

## **Appendix A: Additional Data from the Laboratory Studies**

**Table 1A.** Sorption of Fe on the TNX OD sediment

	Treatment description	Rep.	Initial conc. of Fe <sup>a</sup> [mg/kg]	Initial pH	Initial Eh [mV]	pH after 4 days	Eh after 4 days [mV]	Absorbance [mm]	Final Fe conc. <sup>b</sup> [mg/kg]	Corrected Final Fe conc. <sup>c</sup> [mg/kg]	Kd for total Fe [g/L]	Fe sorbed [µg/g]
0-1	No sediment	1	0.0	6.91	205	6.95	188.4	0.02	-0.219			
0-1	No sediment	2	0.0	7.03	204.5	7.13	191.6	0.02	-0.219			
0-2	No sediment	3	0.0	7.13	200.6	7.1	196.7	0.02	-0.219			
1-1	sediment	1	0.0	6.69	203.3	6.25	217.5	0.0743	0.297			
1-2	sediment	2	0.0	6.65	204.4	6.36	219.5	0.0978	0.348			
1-3	sediment	3	0.0	6.75	204.3	6.33	223	0.0882	0.352			
2-1	sediment	1	0.9	6.62	106.8	6.23	234.9	0.1067	0.445	0.113	141	18
2-2	sediment	2	0.9	6.5	93.5	6.31	234	0.1087	0.458	0.126	124	18
2-3	sediment	3	0.9	6.49	107	6.17	240.5	0.106	0.440	0.108	148	18
3-1	sediment	1	2.3	6.52	93	6.09	244.9	0.1024	0.451	0.119	363	45
3-2	sediment	2	2.3	6.49	86.3	6.13	249.5	0.1026	0.512	0.180	232	44
3-3	sediment	3	2.3	6.53	89.9	6.18	248.2	0.1012	0.443	0.111	393	46
4-1	sediment	1	4.6	6.38	86.7	6.08	268	0.1271	0.577	0.245	353	89
4-2	sediment	2	4.6	6.41	86.1	6.04	271.6	0.1143	0.494	0.162	546	91
4-3	sediment	3	4.6	6.41	85.7	6.01	267.1	0.1232	0.552	0.220	396	89
5-1	sediment	1	13.8	6.11	85.1	5.71	266.9	0.1053	0.534	0.202	1343	273
5-2	sediment	2	13.8	6.1	87.2	5.74	242.3	0.1453	0.624	0.292	919	270
5-3	sediment	3	13.8	6.15	84.2	5.71	259.3	0.103	0.515	0.183	1481	274
6-1	sediment	1	23.0	5.93	92.5	5.32	215.3	0.1238	0.601	0.269	1683	455
6-2	sediment	2	23.0	6.02	84.4	5.34	211.6	0.1139	0.532	0.200	2280	457
6-3	sediment	3	23.0	5.97	91.5	5.35	202	0.1139	0.532	0.200	2273	456

a Initial concentration of Fe in each treatment was based on the spike solution Fe concentration (368 mg/kg)

b The final Fe concentration was calculated from the calibration equation (Figure 1A)

c The final Fe concentration was corrected for a background concentration of Fe from the sediment B5 from the TNX OD and from the TNX OD water

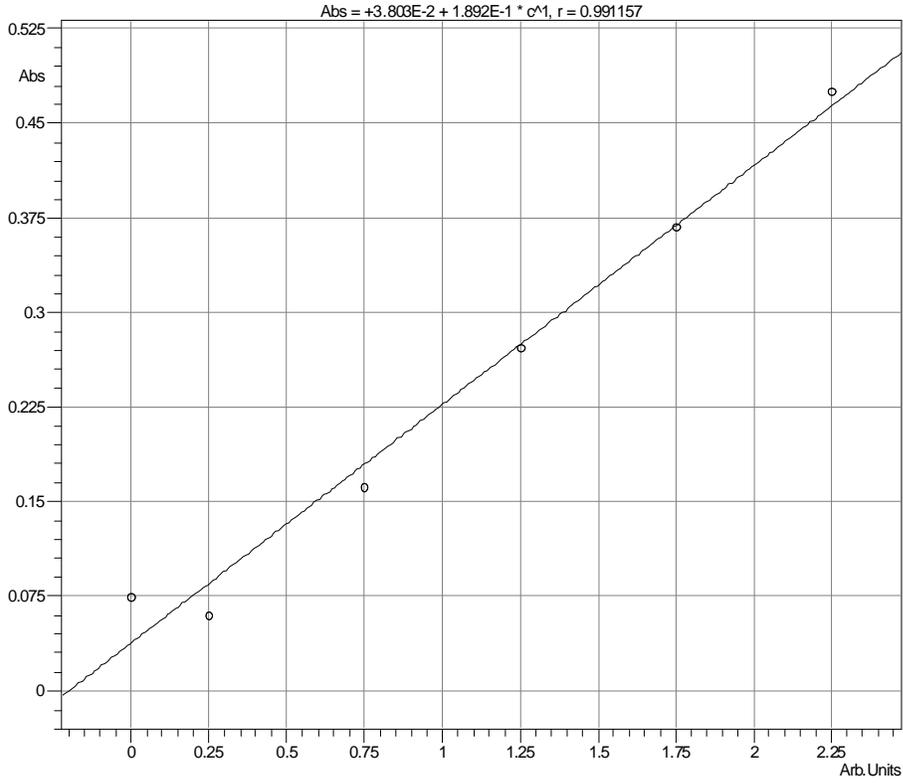
**Table 2A.** Sorption of P on the TNX OD sediment

Treat ment	Treatment description	Initial con. of added P <sup>a</sup> [mg/kg]	Initial pH	Final pH	Absorbance	Final P conc. <sup>b</sup> [mg/kg]	Kd for P [g/L]	P sorbed [mg/kg]
I	No sediment		6.98	7.03	0.0137	0.073		
I	No sediment		6.99	7.06	0.0459	0.466		
I	No sediment		7.02	7.08	0.0086	0.011		
II	Sediment	0.95	6.73	6.63	0.0625	0.852	1.9	1.6
II	Sediment	0.95	6.69	6.3	0.0174	0.302	35.5	10.7
II	Sediment	0.95	6.67	6.28	0.0303	0.459	17.7	8.1
III	Sediment	1.72	6.68	6.3	0.0847	1.122	8.7	9.8
III	Sediment	1.72	6.64	6.3	0.0111	0.225	109.6	24.6
III	Sediment	1.72	6.59	6.31	0.0129	0.247	98.4	24.3
IV	Sediment	4.02	6.59	6.28	0.0585	0.803	65.9	52.9
IV	Sediment	4.02	6.6	6.32	0.012	0.236	263.9	62.2
IV	Sediment	4.02	6.65	6.31	0.012	0.236	264.7	62.4
V	Sediment	7.85	6.56	6.37	0.0228	0.367	336.0	123.5
V	Sediment	7.85	6.57	6.35	0.0807	1.074	104.1	111.8
V	Sediment	7.85	6.63	6.3	0.0294	0.448	272.1	121.9
VI	Sediment	19.35	6.54	6.47	0.0649	0.881	345.6	304.4
VI	Sediment	19.35	6.55	6.45	0.0741	0.993	304.2	302.1
VI	Sediment	19.35	6.57	6.36	0.0871	1.152	260.2	299.7
VII	Sediment	38.51	6.55	6.34	0.2735	3.425	169.0	578.7
VII	Sediment	38.51	6.51	6.37	0.3317	4.135	137.5	568.4
VII	Sediment	38.51	6.43	6.37	0.2391	3.005	194.8	585.3
VIII	Sediment	76.84	6.41	6.37	0.8699	10.698	101.9	1090.4
VIII	Sediment	76.84	6.38	6.35	0.8956	11.011	98.5	1084.7
VIII	Sediment	76.84	6.35	6.32	0.8644	10.631	102.9	1094.2

a Initial concentration of P in each treatment was based on the P spike solution concentration (507mg/kg)

b The final P concentration was calculated from the calibration equation (Figure 2)

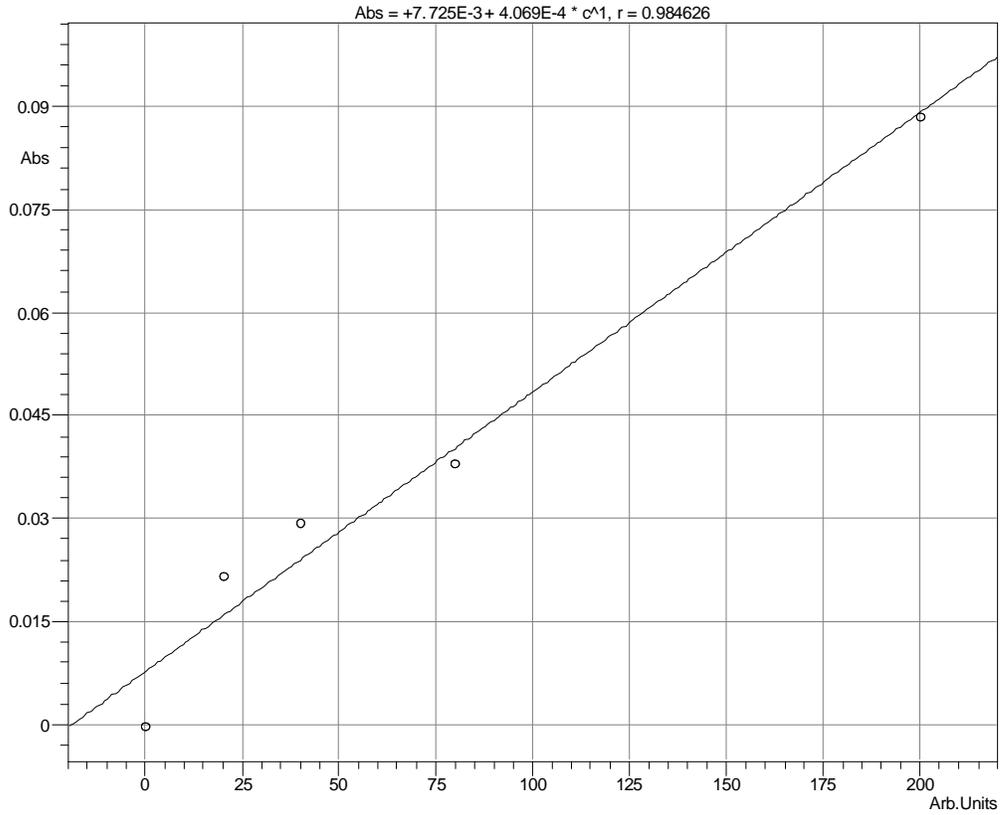
**Figure 1A.** The calibration equation for Fe absorbance



Concentration of Fe (total) in mg/kg.

No.	Name	Conc. mg/kg	Fact Value or [Abs]
1	1-1A	0	1 0.0743
2	250MG/KG	0.25	1 0.0598
3	750MG/KG	0.75	1 0.1615
4	1250MG/K G	1.25	1 0.2721
5	1750MG/K G	1.75	1 0.3679
6	2250PPB	2.25	1 0.475

**Figure 2 A.** The calibration equation for P absorbance



Standard	Conc. P (ppb)	Dilution Factor	Value (Arb.Units)
BLANK	0	1	-0.0003
20 PPB	20	1	0.0217
40 PPB	40	1	0.0293
80 PPB	80	1	0.0378
120 PPB	120	1	0.0817
200 PPB	200	1	0.0884

## **Appendix B: Work Instructions for the Laboratory Studies**

## Phosphorous Sorption Isotherm

**Objective:** The objective of the phosphate sorption isotherm experiments was to measure the phosphate distribution coefficient,  $K_d$ , in the TNX OD sediment (from coordinate B5) to permit calculation of the effective diffusion coefficient,  $D_{eff}$ , was used the Fick's second law describing one-dimensional diffusion of solutes in soil as (Dragun, 1998):

$$\delta c / \delta t = (D_{eff} / R_F) (\delta^2 c / \delta x^2) \quad (1)$$

$c$  = concentration of a solute ( $\text{mg}/\text{cm}^3$ )

$t$  = time (s)

$D_{eff}$  = measured diffusion coefficient ( $\text{cm}^2/\text{s}$ ),

$R_F$  = retardation factor (calculated from Equation 2)

$X$  = direction of diffusion (cm)

$$R_F = 1 + (\rho_b / \phi_e) K_d \quad (2)$$

$\rho_b$  = the porous media bulk density ( $\text{mass}/\text{length}^3$ ) (taken from literature for a sediment with the texture of sediment B5, loamy sand,  $1.55 \text{ g}/\text{cm}^3$ ) (Dragun, 1998)

$\phi_e$  = the effective porosity at saturation of media (taken from literature for a sediment with the texture of sediment B5, loamy sand, 0.47) (Hillel, 1980)

$$D_e = D_o / R_F \quad (3)$$

$D_e$  = measured diffusion coefficient,

$D_o$  = the aqueous diffusion coefficient (taken from literature),

$R_F$  = retardation factor (calculated from Equation 2)

### Solutions:

1. 0.01 M NaCl = 0.52 g/L
2. 400 mg/kg Stock P Solution = 0.585 g/L  $\text{NaH}_2\text{PO}_4\text{-H}_2\text{O}$

### Method:

1. Label 50-ml centrifuge tubes as shown in Table 1.
2. Add 2-g of well mixed B-5 sediment to each tube. Record tube tare weight and actual sediment weight.
3. Pre-equilibrate sediment with 2 3-hr washes followed by a 1 overnight 40-mL wash with 0.01 M NaCl solution. Centrifuge between wash steps. Be sure that no sediment is loss between centrifuge steps, i.e., error on the side of leaving too much liquid in tube rather than losing any solids. Record final wet weight.
4. Add appropriate volumes of NaCl and Stock P Solution to tubes as shown in Table 1.
5. Measure initial pH.
6. Leave samples on platform shaker for 4 days.
7. Measure final pH.
8. Centrifuge. Then measure P concentration of aqueous phase using the Murphy-Riley method as modified by Kuo (1996).<sup>1</sup>
9. Calculate  $K_d$  or Freundlich terms, whichever is appropriate.

<sup>1</sup> Kuo, S. 1996. Phosphorus. In: D. Sparks (ed.) Methods of Sediment Analysis, Part 3 – Chemical Methods. p 859-921. Sediment Science of America, Inc., Madison, WI.

**Table 1B.** Sample identification.

Tube ID#	P Treatment (mg/L)	Rep.	Tube Tare Wt. (g)	Sediment Dry Wt. (g)	Sediment Wet Wt. (g)	0.013 M NaCl Added (mL)	400-mg/kg Stock PSoln. Added (mL)	Initial pH	Final pH
0-1	0	1				40	0		
0-2	0	2				40	0		
0-3	0	3				40	0		
1-1	1	1				39.9	0.1		
1-2	1	2				39.9	0.1		
1-3	1	3				39.9	0.1		
2.5-1	2.5	1				39.75	0.25		
2.5-2	2.5	2				39.75	0.25		
2.5-3	2.5	3				39.75	0.25		
5-1	5	1				39.5	0.5		
5-2	5	2				39.5	0.5		
5-3	5	3				39.5	0.5		
12.5-1	12.5	1				38.75	1.25		
12.5-2	12.5	2				38.75	1.25		
12.5-3	12.5	3				38.75	1.25		
25-1	25	1				37.5	2.5		
25-2	25	2				37.5	2.5		
25-3	25	3				37.5	2.5		
50-1	50	1				35	5		
50-2	50	2				35	5		
50-3	50	3				35	5		

## Ferrous Iron Sorption Isotherm

### Solutions:

3. 400 mg/kg Stock  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  Solution = 0.7117 g of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  in 500 mL  $\text{H}_2\text{O}$

Calculated as followed:

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  FW=198.746 g/mol

Ratio of Fe/  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  =  $1/0.281 = 3.559$

We need 200 mg of  $\text{Fe}^{2+}$  in 500 ml of water to make 400 mg/kg  $\text{Fe}^{2+}$  solution:

$200 \text{ mg} \times 3.559 = 711.7 \text{ mg } \text{FeCl}_2 \cdot 4\text{H}_2\text{O}$

### Method:

10. Label 50-ml centrifuge tubes as shown in Table 1.
11. Add 2-g of well mixed B5 sediment to each tube. Record tube tare weight and actual sediment weight.
12. Pre-equilibrate sediment with 2 3-hr washes followed by a 1 overnight 40-mL wash with the TNX OD swamp water. Centrifuge between wash steps. Be sure that no sediment is loss between centrifuge steps, i.e., error on the side of leaving too much liquid in tube rather than losing any solids. Record final wet weight.
13. Add appropriate volumes of swamp water from the TNX OD and Stock  $\text{FeCl}_2$  Solution to tubes as shown in Table 1.
14. Measure initial pH and Eh.
15. Leave samples on platform shaker for 4 days.
16. Measure final pH and Eh.
17. Centrifuge. Then measure Fe total and  $\text{Fe}^{2+}$  concentration of aqueous phase by calorimetric determination of ferrous iron and ferric iron by 1,10-phenanthroline method (page 659).
18. Calculate  $K_d$  or Freundlich terms, whichever is appropriate.

### 1,10 Phenanthroline method (or EPA methods: $\text{Fe}^{2+}$ : EPA#FM3500 and Total Fe: EPA#200.7)

#### Special Apparatus:

Visible or ultraviolet (UV)/visible spectrophotometer

#### Reagents:

1. Ammonium acetate ( $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ ), 5 M.
2. Hydroxylamine hydrochloride ( $\text{NH}_2\text{OH} \cdot \text{HCl}$ ), 10% (10 g  $\text{NH}_2\text{OH} \cdot \text{HCl}$  dilute to 100 mL total volume with deionized water).
3. 1,10-phenanthroline reagent. Dissolve 0.30 g of 1,10-phenanthroline monohydrate in water by heating the mixture to 80°C. Cool the solution and add water to a final volume of 100 mL.
4. Hydrochloric acid, 6 M.
5. Standard Fe solution, 100 mg  $\text{Fe L}^{-1}$ .
6. Standard Fe solutions, 5 mg $\text{L}^{-1}$ . Add 10 mL of 18 M  $\text{H}_2\text{SO}_4$  to 50.0 mL of standard Fe solution having 100 mg  $\text{L}^{-1}$  of Fe, and dilute the solution to 1 L with deionized water.

**Table 2B.** Sample identification, Ferrous Fe sorption Isotherm exp.

Treat ment ID#	Tube ID #	Fe <sup>2+</sup> Treat- ment (mg/ L)	Rep.		Tube Tare Wt. (g)	Sediment Dry Wt. (g)	TNX swamp water Added (mL)	400- mg/kg Stock Fe <sup>2+</sup> Soln. Added (mL)
0	0-1	0	1	No sediment	11.6467	-	40	0
0	0-1	0	2	No sediment	11.6842	-	40	0
0	0-2	0	3	No sediment	11.7733	-	40	0
1	1-1	0	1	Sediment	11.7092	2.0088	40	0
1	1-2	0	2	Sediment	11.7147	2.0073	40	0
1	1-3	0	3	Sediment	11.6449	2.0074	40	0
2	2-1	1	1	Sediment	11.6970	2.0042	39.900	0.1
2	2-2	1	2	Sediment	11.7663	2.0022	39.900	0.1
2	2-3	1	3	Sediment	11.6417	2.0037	39.900	0.1
3	3-1	2.5	1	Sediment	11.6541	2.0092	39.75	0.25
3	3-2	2.5	2	Sediment	11.7088	2.0070	39.75	0.25
3	3-3	2.5	3	Sediment	11.6413	2.0059	39.75	0.25
4	4-1	5	1	Sediment	11.7677	2.0013	39.5	0.5
4	4-2	5	2	Sediment	11.7413	2.0001	39.5	0.5
4	4-3	5	3	Sediment	11.6786	2.0043	39.5	0.5
5	5-1	15	1	Sediment	11.6519	2.0061	38.5	1.5
5	5-2	15	2	Sediment	11.7342	2.0096	38.5	1.5
5	5-3	15	3	Sediment	11.6850	2.0032	38.5	1.5
6	6-1	25	1	Sediment	11.6630	2.0071	37.5	2.5
6	6-2	25	2	Sediment	11.7428	2.0031	37.5	2.5
6	6-3	25	3	Sediment	11.7442	2.0093	37.5	2.5

## Solubility test of collected apatite samples

March 10, 2003

### Method:

1. Label 50-ml centrifuge tubes as shown in Table 1.
2. Add 1-g of well mixed apatite sample to tube following the experimental design (Table 1). Record tube tare weight and actual weight of each apatite sample.
3. Add 10 ml of DI water to each tube.
4. Measure initial pH. If needed adjust pH to ~7.5.
5. Leave sample on platform shaker for 12 days.
6. Measure final pH.
7. Centrifuge. Then measure P concentration of aqueous phase using the Marphy-Riley method as modified by Kuo (1993).
8. Sub-sample of aqueous phase will be analyzed for 30 elements by ICP-AES.

**Table 3B.** Solubility test of the collected phosphate rocks from different locations.

Number ID	Product name/location	A short name	Replicates	Tube label	Vol. of DI Water [mL]	Duration 12 days
1	Phosphate rock	PR-FL	1	PR-FL-1	10	12
	Florida		2	PR-FL-2	10	12
			3	PR-FL-3	10	12
2	Montana Natural Granulated	GRP-MT	1	GRP-MT-1	10	12
	Rock Phosphate		2	GRP-MT-2	10	12
	Montana		3	GRP-MT-3	10	12
3	Spring Phosphate Powdered	PRP-ID	1	PRP-ID-1	10	12
	Rock Phosphate		2	PRP-ID-2	10	12
	Idaho		3	PRP-ID-3	10	12
4	Volcanaphos- granulated rock	VCP-ID	1	VCP-ID-1	10	12
	Phosphate		2	VCP-ID-2	10	12
	Idaho		3	VCP-ID-3	10	12
5	Tennessee Brown Rock	BR-TN	1	BR-TN-1	10	12
	Tennessee		2	BR-TN-2	10	12
			3	BR-TN-3	10	12
6	Tennessee brown Rock	WPO-TN	1	WPO-TN-1	10	12
	Washed Phosphate Ore		2	WPO-TN-2	10	12
	Tennessee		3	WPO-TN-3	10	12
7	Phosphate rock-ore	WG-IPR	1	WG-IPR-1	10	12
	Rasmussen Ridge Mine		2	WG-IPR-2	10	12
	in Soda Spring, Idaho		3	WG-IPR-3	10	12
8	North Carolina Apatite	NCA	1	NCA-1	10	12
			2	NCA-2	10	12
			3	NCA-3	10	12

## A micro-pipette method<sup>2</sup> of apatite samples from different sources

### Reagents:

5% (NaPO<sub>3</sub>)<sub>13</sub> – 50 ml (needed only 10 ml)

2.5 g of % (NaPO<sub>3</sub>)<sub>13</sub> and dilute to 50 ml with DI water

M NaOH – 50 ml (needed only 10 ml)

2g of NaOH and dilute to 50 ml with DI water

Dispersant Solution

10 ml of 5% % (NaPO<sub>3</sub>)<sub>13</sub> and 10 ml of 1.0 M NaOH in 1 L of DI water

### Samples/Method

4 g sample weights were used with 40 ml of dispersant solution. Samples were placed on the shaker platform and shaking overnight at 55 rev/min.

After dispersing, the samples were removed from the shaker and caps removed after a final shaking. After a settling time of clay fraction (1 hr and 50 minutes) the pipette tip (5 mL) was lowered into the suspension with the hand supported by an appropriately sized block of wood and the sample withdrawn slowly over a period of 5 seconds. The samples were dried in a tared aluminum dish at 105°C, and weighed to the nearest 0.0001g. The sand fraction was sieved from the remaining sediment after clay sampling. For the sand fraction a 270 mesh (53 µm) sieve was used. The sand was washed into tared 50 ml beakers, dried, and weighed. Silt content was estimated as the difference between the sum of the sand and clay, and the initial sample weight.

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<sup>2</sup> Miller, W.P. and M. Miller. 1987. "A Micro-Pipette Method for Sediment Mechanical Analysis." *Communications in Sediment Sci., Plant Anal.* 18(1) 1-15.

**Toxicity Characteristic Leaching Procedure Extraction (TCLP Test)**

Extraction solution

0.1 M glacial acetic acid

0.0643 M NaOH

pH 4.93

Add 600 ml of DI water to a 1 L volumetric flask. Add stir bar and stir. Add 5.7 ml of glacial acetic acid (or acetic acid),  $\text{CH}_3\text{CO}_2\text{H}$ . Add 64.4 ml of 1 M NaOH. Remove stir bar and bring up to 1 L with DI water. Measure pH.

Method

1. Label the centrifuge tubes according to the label list in the Table 5B. Add 2 grams dried apatite material and add 40 mL of TCLP extraction solution.
2. Put the centrifuge tubes on the rotating shaker for 18 hrs.
3. Pass through a disposable 0.45 $\mu\text{m}$  polycarbonate filter.
4. Acidify to 2%  $\text{HNO}_3$ ; add 740 $\mu\text{m}$  concentrated  $\text{HNO}_3$  (this assumes a final sample volume of 37 mL)
5. Send samples for ICP analysis for 22 elements.

**Table 5B.** Toxicity Characteristic Leaching Procedure Extraction (TCLP Test)

Number ID	Product name/location	A short Name	Replicates	Lab Label	Tube wt [g]	Sample net Weight [g]	Volume of extraction sol. [mL]
1	Phosphate rock	PR-FL	1	1-1	11.7566	2.0026	40
	Florida		2	1-2	11.7087	2.0048	40
2	Montana Natural Granulated	GRP-MT	1	2-1	11.7017	2.0029	40
	Rock Phosphate, Montana		2	2-2	11.7197	2.0064	40
3	Spring Phosphate Powdered	PRP-ID	1	3-1	11.7368	2.0013	40
	Rock Phosphate, Idaho		2	3-2	11.7711	2.0045	40
4	Volcanaphos- granulated rock	VCP-ID	1	4-1	11.7562	2.0038	40
	phosphate, Idaho		2	4-2	11.7241	2.0086	40
5	Tennessee Brown Rock	BR-TN	1	5-1	11.7128	2.0033	40
	Tennessee		2	5-2	11.8609	2.0047	40
6	Tennessee brown Rock	WPO-TN	1	6-1	11.7062	2.005	40
	washed Phosphate Ore, TN		2	6-2	11.7274	2.0026	40
7	Phosphate rock-ore	WG-IPR	1	7-1	11.8101	2.0069	40
	Rasmussen Ridge Mine		2	7-2	11.7006	2.0013	40
	in Soda Spring, Idaho						
8	North Carolina Apatite	NCA	1	8-1	11.7136	2.0026	40
			2	8-2	11.7335	2.0066	40
9	Biological Apatite	BA	1	9-1	11.7587	2.0023	40
			2	9-2	11.7196	2.0076	40
10	Blank	0	1	0-1	11.7317		40
	(extraction solution)						

## Laboratory Measurement of Zone-of-Influence (ZOI)

### Vertical application of Fe(0) and apatite

**Objective:** To determine horizontal (lateral) movement of P/and Fe in sediment from the TNX OD (B5) with vertical application of North Carolina Apatite, Biological Apatite and Fe(0) application

The experiment was performed in 60ml syringes; 4cm of saturated sediment (B5, the TNX OD) was placed into the syringe and on the top of the sediment was placed a 1.1cm layer of saturated amendment (apatite or Fe). The syringes were sealed and placed vertically on the lab bench for a period of 3 months. On August 12, 2003 (after 3 months), the bottom of the syringe with the sample was cut off and the sample was gently pushed out and each 0.5cm of pushed sample was collected individually. Each collected slice of sediment and amendment was digested by HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>/HCl and the digested extracts were analyzed for total content of P or Fe by ICP-AES.

#### **The experimental design:**

Four treatments:

- 4 controls:     only sediment (B5) – 4 cm, (label: C-1 B5)
- only biological phosphate (BP) – 1.1 cm (label: C-2 BA)
- only North Carolina Apatite (NCA) – 1.1 cm (label: C-3 NCA)
- only Fe (0) – 1.1 cm (Label: C-4 Fe(0))

Sediment B5(4 cm) and BP (1.1cm) x5 (Labels: 1-1B5/BP.....1-5B5/BA)

Sediment B5 (4 cm) and NCA (1.1cm) x4 (Labels: 2-1 B5/NCA....2-4B5/NCA)

Sediment B5 (4 cm) and Fe(0) (1.1 cm) x4 (Labels: 3-1 B5/Fe(0)....3-4 B5/Fe(0))

**Table 6B.** Laboratory measurement of Zone-of-Influence (ZOI)

Label	Description	Description of sub-samples*							
		Length (cm)/weight(g)							
		A	b	c	d	e	f	g	h
		1 cm	0.2 cm	0.3 cm	0.5 cm	0.5 cm	0.5 cm	1 cm	1 cm
1-1 B5/BP	Sediment B5/								
1-2 B5/BP	Biological Phosphate								
1-3 B5/BP									
1-4 B5/BP									
1-5 B5/BP									
2-1 B5/NCA	Sediment B5/								
2-2 B5/NCA	North Carolina Apatite								
2-3 B5/NCA									
2-4 B5/NCA									
3-1 B5/Fe(0)	Fe (0)								
3-2 B5/Fe(0)									
3-3 B5/Fe(0)									
3-4 B5/Fe(0)									
C-1 B5	4cm								
C-2 BA	1.1 cm								
C-3 NCA	1.1 cm								
C-4 Fe(0)	1.1 cm								

\* Each sample was divided as the following: 1 cm slice (amendment - slice a); 0.2 cm slice (interlayer - amendment/sediment B5 - slice b); 0.3 cm slice of sediment (c); 0.5 cm slice of sediment (d, e, and f); 1.0 cm slice of sediment (g and h).

**Appendix C: Work Instructions and Additional Results for the  
Field Study**

**Work Instructions**  
**Sediment Amendment Study at TNX OD Outfall Delta**  
**ERD-EN-2002-0099 Rev. 0**

**Approvals**

_____	_____	Date _____
Print	Signature	
	Project Task Team Lead (PTTL)	
_____	_____	Date _____
Print	Signature	
	SRTC Study Lead	
_____	_____	Date _____
Print	Signature	
	Person-In-Charge (PIC)	
_____	_____	Date _____
Print	Signature	
	ER RCO	

**Additional Reviewers**

_____	_____	Date _____
Print	Signature	
	Title: Technical Oversight/Health and Safety Officer	
_____	_____	Date _____
Print	Signature	
	Title: _____	
_____	_____	Date _____
Print	Signature	
	Title: _____	
_____	_____	Date _____
Print	Signature	
	Title: _____	

## **PURPOSE**

These Work Instructions identify and describe Scope, Safety, Special Instructions, Prerequisites, Work Steps, Radiological Action Steps and clearance activities for performing the study as described in the “Technical Task Plan for Proof-of-principle Laboratory Study of Effects of Sediment Amendments on Contaminant Immobilization in TNX Outfall Delta Sediments and Zone of Influence Field Treatability Study of Sediment Amendments in TNX Outfall Delta Sediments.”

## **SCOPE**

Personnel will perform sediment sampling and introduce amendments to the sediment at depths not exceeding 12 inches in accordance with the “Technical Task Plan for Proof-of-principle Laboratory Study of Effects of Sediment Amendments on Contaminant Immobilization in TNX Outfall Delta Sediments and Zone of Influence Field Treatability Study of Sediment Amendments in TNX Outfall Delta Sediments.” Radiological surveillance will be provided to ensure worker protective measures are adequate and to ensure radiological controls are heeded. The location of this study is at the TNX Outfall Delta the area is posted as a Sediment Contamination Area (SCA) and a Controlled Area.

## **SAFETY**

- Personnel shall comply with all applicable safety standards, procedures and practices for the job and area.
- A pre-job briefing is required prior to performing any work. These work instructions will be used for the initial sampling and study set up and subsequent sampling for study results, a pre-job briefing will be required for each and every event.
- Worker notification should be via radio to KIJ5 or equivalent. Other equivalent means of communication may be employed to achieve emergency notification.
- Personnel will maintain awareness of uneven terrain, embankments, slopes, loose rocks and tripping hazards.
- Maintain awareness of poisonous plants, animals and insects.
- Additional safety precautions shall be taken as noted in the Work Package Documentation and Site Specific Health and Safety Plan (SSHASP) (Q-SHP-2002-00037).
- Workers shall be cognizant to the symptoms of heat stress and maintain awareness of workers and themselves for the symptoms of heat stress.

## **PREREQUISITIES**

- Pre-Job Briefing.
- RCO is to be notified prior to entry to the SCA.
- Radiological Worker Training II for all workers donning radiological protective clothing.
- Radiological Work Permit (RWP) 02ER-001 for Radioactive Material Area (RMA) access (if needed) and Restricted Radiological Use Only (RRUO) vehicle operation
- Radiological Work Permit (RWP) 02ER-002 for tasks requiring donning of Radiological Use gloves, such as sediment sampling, withdrawing items from subsurface sediments (i.e., items that have penetrated the ground surface), and decontamination of tools.

- An RMA will be established or designated if required. The RCO FM approval for a new RMA must be obtained prior to installation.
- Rad launderable Personal Protective Equipment (PPE) to include rubber gloves and rubber shoecovers or boots (for wet field conditions).
- PPE shall be staged near the work site in advance.
- Receptacles shall be established to receive radiological protective clothing. Sedimented/used Radiological Use PPE containers will be radiologically surveyed, labeled/tagged and removed from the area and transported to the ERD Laundry Station each day. No radiological laundry will be left unattended in the field.

**SPECIAL INSTRUCTIONS**

- Hazardous Material Transportation Representative (HMTR) approval for transport of samples field screened at  $<2\text{nCi/g}$  total alpha/beta/gamma activity has been obtained for transport of radiological materials on site roads and on and across Highway 125. HMTR must be contacted if total activity  $>2\text{nCi/g}$ .
- Stage supplies and equipment outside the SCA. Do not bring unnecessary items into the SCA.
- Items, materials or samples designated or suspected as being radioactive material shall be stored or staged in an RMA or under continuous control by a qualified radiological worker.
- Continuous RCO radiological surveillance is required for sampling or withdrawing items from subsurface sediments (i.e., items that have penetrated the ground surface).
- RCO is to be notified prior to moving the RRUO vehicle outside a controlled area.
- Personnel shall be monitored by RCO after removing radiological PPE.
- If unexpected radiological conditions are encountered or radiological posting boundaries must be modified, RCO shall notify RCO First Line Manager and PIC of situation immediately, after a safe condition has been established.
- RCO shall perform radiological surveys of the equipment for the purpose of uncontrolled radiological release at conclusion of job evolution. Surfaces of equipment shall be dry, industrially clean and free of vegetation and sediment prior to radiological survey.

**CONTACTS**

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Darren Gillis	Waste Management Lead	952-6504 Beeper 15675
Greg Joyner	ER RCO First Line Manager	952-7927 Beeper 11895
Cathy Madore	ERD SIRIM Coordinator	952-6656 Beeper 19365
Laura Bagwell	Technical Oversight/Health & Safety Officer	952-6787 Beeper 17370
Sallie Cooks	RRUO Vehicle Operator (sample delivery)	952-6704 Beeper 14728

**WORK STEPS AND INSTRUCTIONS**

Work Step	Work Instructions for Outfall Delta Sampling
1	If not previously performed, request approval from RCO Facility Manager for RRUO designation of sample transport vehicle in accordance with 5Q1.1-522. Ensure vehicle RRUO tag is current. Establish laundry and waste (if waste is generated) receptacles at the work site.
2	Contact RCO for coverage prior to any intrusive work in the Outfall Delta SCA.
	The statistical design of this experiment is a randomized complete block ( <b>Figure 1</b> ). There are 3 replicates (blocks) and 7 treatments (control, horizontal Fe(0), vertical Fe(0), horizontal apatite, vertical apatite, horizontal apatite + Fe(0), and a vertical apatite + Fe(0)). The experiment will be located between markers A-5 and A-6 in a flat, vegetation-free area of 480- x 180-cm. Mark the 4 corners of experimental plots with permanent stakes. Use flags to locate corners of 30 x 30 cm plots. A 45-cm buffer zone (area between treatments) will exist between all plots.
3	Obtain and prepare samples in accordance with the Technical Task Plan. Using a ¾-inch diameter stainless steel auger with a plastic liner, recover a 30-cm core from the center of the plot. Remove the liner from the auger, put end caps and label liner as described in <b>Table 1</b> . Before proceeding to next location, rinse dirt off auger by squirting distilled-water onto the auger and rubbing the auger with gloves. Include 2 duplicates, i.e., 1 duplicate for about every 10 samples. Include 1 field blank control. All samples will be logged in the SRTC Field Sample Logbook.
RCO Action Step 1	Perform radiological surveys during sampling and when items are withdrawn from the sediment subsurface. Ensure samples are packaged in accordance with radioactive material requirements. Identify and label accordingly. If contamination or radioactivity is found above RWP suspension guides or above RBA posting limits, inform workers to establish a safe condition, suspend work, monitor personnel, post in accordance with procedure 5Q1.2. 518 and inform RCO Management and PIC immediately.
4	Apply treatments to plots as described in <b>Table 2 C</b> . Repeat work step 3, RCO Action Step 1, and work step 4 as necessary to accomplish all sampling and sediment amendment application as described in <b>Tables 1C and 2C</b> .
5	Items to be removed from the sampling area (for unconditional release) will be prepared for radiological survey by ensuring they are industrially clean, all assessable areas have been exposed and unconditional release documentation has been prepared. Rinsate may fall to ground at sample location. Return sample area to pre-sampling condition. Dispose of any generated waste in accordance with Waste Management Requirements.
RCO Action Step 2	RCO shall perform radiological release survey of equipment (including vehicles, if applicable) and materials for the purpose of unconditional radiological release. Inform work group of radiological status of items or

	equipment.
6	If radiological surveys so indicate, decontaminate items and equipment. Dispose of any generated waste in accordance with Waste Management Requirements.
7	Repeat work step 5, RCO Action Step 2 and work step 6 until all items and equipment (including RRUO vehicles, if applicable) meet the criteria for unconditional release. If unconditional release criteria can not be met, inform RCO management and PIC of radiological status of item or equipment. NOTE: Items not meeting the criteria for unconditional radiological release shall be contained and identified as radioactive material and stored in an RMA. It may be necessary to move so designated radioactive material to another site location with an RRUO vehicle.
RCO Action Step 3	RCO shall perform radiological surveys as necessary with the goal of returning the sample area to its radiological status prior to sampling (SCA). Inform RCO management and PIC of radiological conditions before changing posting and upon completion of this reposting. IF conditions for SCA Radiological Posting can not be met, inform RCO FLM and PIC of radiological status and conditions of area.
8	Ensure all equipment, materials, waste (if any) or other items has been removed from the SCA unless stored in an approved RMA.

Figure 1 C. Experimental Plot Design

	Row A 30 cm	45 cm	Row B 30 cm	45 cm	Row C 30 cm	45 cm	Row D 30 cm	45 cm	Row E 30 cm	45 cm	Row F 30 cm	45 cm	Row G 30 cm
Replicate 1	30-cm Vertical Apatite		Vertical Ap + Fe(0)		Vertical Fe(0)		Hori Ap + Fe(0)		Hori Apatite		Hori Fe(0)		Control
	45-cm												
Replicate 2	30-cm Vertical Fe(0)		Hori Ap + Fe(0)		Vertical Apatite		Hori Fe(0)		Control		Vertical Ap + Fe(0)		Hori Apatite
	45-cm												
Replicate 3	30-cm Vertical Apatite		Vertical Fe(0)		Hori Ap + Fe(0)		Vertical Ap + Fe(0)		Hori Apatite		Control		Hori Fe(0)

Table 1 C. Sample Identification

Sample Code	EMS/EGG Sample Logbook Number	Sample Description
C-I-0	900101	Control, Replicate 1, Time Zero
C-II-0	900102	Control, Replicate 2, Time Zero
C-III-0	900103	Control, Replicate 3, Time Zero
HA-I-0	900104	Horizontal Apatite, Replicate 1, Time Zero
HA-II-0	900105	Horizontal Apatite, Replicate 2, Time Zero
HA-III-0	900106	Horizontal Apatite, Replicate 3, Time Zero
HAF-I-0	900107	Horizontal Apatite + Fe(0), Replicate 1, Time Zero
HAF-II-0	900108	Horizontal Apatite + Fe(0), Replicate 2, Time Zero
HAF-II-0-dup	900109	Horizontal Apatite + Fe(0), Rep. 2, Time Zero, Duplicate
HAF-III-0	900110	Horizontal Apatite + Fe(0), Replicate 3, Time Zero
HF-I-0	900111	Horizontal Fe(0), Replicate 1, Time Zero
HF-II-0	900112	Horizontal Fe(0), Replicate 2, Time Zero
HF-III-0	900113	Horizontal Fe(0), Replicate 3, Time Zero
VA-I-0	900114	Vertical Apatite, Replicate 1, Time Zero
VA-II-0	900115	Vertical Apatite, Replicate 2, Time Zero
VA-III-0	900116	Vertical Apatite, Replicate 3, Time Zero
VAF-I-0	900117	Vertical Apatite + Fe(0), Replicate 1, Time Zero
VAF-II-0	900118	Vertical Apatite + Fe(0), Replicate 2, Time Zero
VAF-III-0	900119	Vertical Apatite + Fe(0), Replicate 3, Time Zero
VF-I-0	900120	Vertical Fe(0), Replicate 1, Time Zero
VF-II-0	900121	Vertical Fe(0), Replicate 2, Time Zero
VF-II-0-dup	900122	Vertical Fe(0), Replicate 3, Time Zero
VF-III-0	900123	Vertical Fe(0), Replicate 3, Time Zero
Field blank	900124	Field Blank: empty sample containers; no sediment collection; check on cross contamination and aerial deposition

**Table 2C.** Treatment Description

<b>Treatment</b>	<b>Description</b>
Control	Add nothing
Horizontal Apatite	Surface apply 163-g Apatite
Horizontal Apatite + Fe(0)	Surface apply 163-g Apatite + 163-g Fe(0)
Horizontal Fe(0)	Surface apply 163-g Fe(0)
Vertical Apatite	Pack 115 g Apatite into existing “sample” hole ( $\frac{3}{4}$ -diameter, 30-cm deep) using stainless steel rod.
Vertical Apatite + Fe(0)	Pack 115 g Apatite and 400-g Fe(0) into two existing “sample” holes (each $\frac{3}{4}$ -diameter, 30-cm deep) using stainless steel rod
Vertical Fe(0)	Pack 400-g Fe(0) into existing “sample” hole ( $\frac{3}{4}$ -diameter, 30-cm deep) using stainless steel rod

**Table 3C.** Sediment samples taken from the TNX OD before the application of the amendments

<b>Treatment</b>	<b>Sample code</b>	<b>EMS/EG G sample Logbook Number</b>	<b>Sample length [inch]</b>	<b>Hole depth vertical treatment</b>	<b>Amount of applied amendment [g]</b>
Control	C-I-0	900101			0
Horizontal apatite	HA-I-0	900104	3 1/2		163
Horizontal Fe(0)	HF-I-0	900111	4 1/2		163
Control	C-II-0	900102	4		0
Vertical Apatite & Fe(0)	VAF-I-0	900117	3 1/2	5	62.6A/219Fe
Horizontal Fe(0)	HF-II-0	900112	2 3/4		163
Horizontal Apatite	HA-II-0	900115	3 1/2		163
Control	C-III-0	900103	2 1/2		0
Horizontal apatite	HA-III-0	900106	3 1/4		163
Vertical Apatite & Fe(0)	VAF-II-0	900118	3 1/2	3 1/2	41.7A/145.9Fe
Horizontal Fe(0)	HF-III-0	900113	3		163
Horizontal Apatite & Fe(0)	HAF-I-0	900107	3 7/8		163 A&163 Fe
Vertical Fe(0)	VF-I-0	900120	2 7/8	4	400
Vertical Apatite	VA-I-0	900114	2 5/8	4	58.6
Horizontal Apatite & Fe(0)	HAF-II-0	900108	4 1/4		163 A&163 Fe
Vertical Fe(0)	VF-II-0	900121	3	4 1/8	400
Horizontal Apatite & Fe(0)	HAF-III-0	900109	2 5/8		163 A&163 Fe
		900110	2 5/8		
Horizontal Apatite & Fe(0)	HAF-IV-0	900119	3 1/8		115A/400Fe
Vertical Apatite	VA-II-0	900115	2 7/8	3 7/8	54 2/7
Vertical Fe(0)	VF-III-0	900122	3 3/8		400
		900123	3 3/8	5 1/8	
Vertical Apatite	VA-III-0	900116	6 7/8	9 1/2	115
Vertical Apatite & Fe(0)	VAF-III-0	900125	2 7/8		22.7A/79.3Fe
Field blank		900124			

**Measurement of Zone-of-Influence (ZOI) based on the field samples**

The objective of this study was to determine the ZOI of Fe(0) and two types of apatite in the TNX OD sediment after 13 months of their application.

**Table 4C.** Treatment description

Application date	Treatment	Description
8/8/02	Control	Add nothing
8/8/02	Horizontal Biological Phosphate (BP)	Surface apply 163 g of BP
8/8/02	Horizontal BP + Fe(0)	Surface apply of 163 g of BP and 163g of Fe(0)
8/8/02	Horizontal Fe(0)	Surface apply of 163 g Fe (0)
8/22/02	Horizontal North Carolina Apatite NCA	Surface apply of 163 g of NCA
11/7/02	Horizontal NCA + Fe (0)	Surface supply of 163 g of NCA and 163 of Fe(0)
8/8/02	Vertical BP	Packed 59g/54g/115g of BP into a hole
8/8/02	Vertical Ba + Fe (0)	Packed 63BP/219Fe(0); 42BA/146Fe(0); 23BA/79Fe(0)
8/8/02	Vertical Fe (0)	Packed 400g/400g/400g of Fe(0)
8/22/02	Vertical NCA	Packed 210g/111g/114g of NCA
11/7/02	Vertical NCA +Fe(0)	Packed

Treatments with horizontal application of Fe(0) and two types of apatite (North Carolina Apatite and Biological Phosphate):

There are 5 horizontal treatments (Table 1) with three replicates in each (total number of plots 15) and one control treatment (three replicates).

Sediment samples from the horizontal treatments were collected with a sediment sampler into plastic sleeves (~1 inch diameter; sampling depth ~ 5 inches).

The sediment samples were collected from the center of each plot (next to the hole after the first sediment sampling). Collected sediments were sliced (every 1cm) and each slice was analyzed for the following:

pH

Total concentrations of P or Fe in the extracts from a total digestion with HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>/HCl were analyzed by ICP-AES.

Treatments with vertical application of Fe(0) and two types of apatite (North Carolina Apatite and Biological Phosphate):

There are 5 vertical treatments (Table 1) with three replicates in each (total number of plots is 15). Sediment samples from these treatments were collected from the center of each plot (next to the hole after the first sediment sampling) using a sediment profiler (7" deep x 4" wide and 1" thick). The collected sediment profile was divided vertically into 1 cm wide strips. Each strip was analyzed for pH and P or Fe accordingly to the treatment.

**Table 5C.** Sampling Plan After 13 Months of Amendments Application

<b>SRTC ID#</b>	<b>Treatment Label</b>	<b>Amendment</b>	<b>Type of Application</b>	<b>Sub-sample Labels</b>	<b>Sampling Tool</b>
1	Control-I	None	Horizontal	1A, 1B, 1C*	sediment sampler
2	Control-II	None	Horizontal	2A, 2B, 2C	sediment sampler
3	Control-III	None	Horizontal	3A, 3B, 3C	sediment sampler
4	Control-I	None	Vertical	4a, 4b, 4c, 4d,....	sediment profiler
5	Control-II	None	Vertical	5a, 5b, 5c, 5d....	sediment profiler
6	Control-III	None	Vertical	6a, 6b, 6c, 6d...	sediment profiler
7	H-NCA-I	North Carolina Apatite	Horizontal	7A, 7B, 7C	sediment sampler
8	H-NCA-II	North Carolina Apatite	Horizontal	8A, 8B, 8C	sediment sampler
9	H-NCA-III	North Carolina Apatite	Horizontal	9A, 9B, 9C	sediment sampler
10	V-NCA-I	North Carolina Apatite	Vertical	10a, 10b, 10c, ...	sediment profiler
11	V-NCA-II	North Carolina Apatite	Vertical	11a, 11b, 11c...	sediment profiler
12	V-NCA-III	North Carolina Apatite	Vertical	12a, 12b, 12c...	sediment profiler

13	H-BP-I	Biological Phosphate	Horizontal	13A, 13B,13C	sediment sampler
14	H-BP-II	Biological Phosphate	Horizontal	14A, 14B, 14C	sediment sampler
15	H-BP-III	Biological Phosphate	Horizontal	15A, 15B, 15C	sediment sampler
16	V-BP-I	Biological Phosphate	Vertical	16a, 16b, 16c...	sediment profiler
17	V-BP-II	Biological Phosphate	Vertical	17a, 17b, 17c....	sediment profiler
18	V-BP-III	Biological Phosphate	Vertical	18a, 18b, 18c....	sediment profiler
19	H-Fe-I	Fe(0)	Horizontal	19A, 19B. 19C	sediment sampler
20	H-Fe-II	Fe(0)	Horizontal	20A, 20B, 20C	sediment sampler
21	H-Fe-III	Fe(0)	Horizontal	21A, 21B, 21C	sediment sampler
22	V-Fe-I	Fe(0)	Vertical	22a, 22b, 22c ...	sediment profiler
23	V-Fe-II	Fe(0)	Vertical	23a, 23b, 23c...	sediment profiler
24	V-Fe-III	Fe(0)	Vertical	24a, 24b, 24c...	sediment profiler
25	H-NCA/Fe-I	North Carolina Apatite/Fe(0)	Horizontal	25A, 25B, 25C	sediment sampler
26	H-NCA/Fe-II	North Carolina Apatite/Fe(0)	Horizontal	26A, 26B, 26C	sediment sampler
27	H-NCA/Fe-III	North Carolina Apatite/Fe(0)	Horizontal	27A, 27B, 27C	sediment sampler

28	V-NCA/Fe-I	North Carolina Apatite/Fe(0)	Vertical	28a, 28b, 28c...	sediment profiler
29	V-NCA/Fe-II	North Carolina Apatite/Fe(0)	Vertical	29a, 29b, 29c...	sediment profiler
30	V-NCA/Fe-III	North Carolina Apatite/Fe(0)	Vertical	30a, 30b, 30c....	sediment profiler
31	H-BP/Fe-I	Biological Phosphate/Fe(0)	Horizontal	31A, 31B, 31C	sediment sampler
32	H-BP/Fe-II	Biological Phosphate/Fe(0)	Horizontal	32A, 32B, 32C	sediment sampler
33	H-BP/Fe-III	Biological Phosphate/Fe(0)	Horizontal	33A, 33B, 33C	sediment sampler
34	V-BP/Fe-I	Biological Phosphate/Fe(0)	Vertical	34a, 34b, 34c.....	sediment profiler
35	V-BP/Fe-II	Biological Phosphate/Fe(0)	Vertical	35a, 35b, 35c....	sediment profiler
36	V-BP/Fe-III	Biological Phosphate/Fe(0)	Vertical	36a, 36b, 36c...	sediment profiler
37	H-NCA-I d*	North Carolina Apatite	Horizontal	37A, 37B, 37C	sediment sampler
38	H-NCA/Fe-II d	North Carolina Apatite/Fe(0)	Horizontal	38A, 38B, 38C	sediment sampler
39	V-BP/Fe-Id	Biological Phosphate/Fe(0)	Vertical	39a, 39b, 39c	sediment profiler
40	H-Fe-III d	Fe(0)	Horizontal	40A, 40B, 40C	sediment sampler

\*d- duplicate

\*\*A, B, C, .....- the uppercase letters stand for split samples in the horizontal treatments; 1 cm slices or if possible 0.5 cm slices

\*\*\*a, b, c, d, e, f, g, h,....the lowercase letters stand for split samples in the vertical treatments; 1 cm layers

**Total Digestion of the sediment samples from the TNX OD**

A total digestion of the sediment from the TNX OD from vertical and horizontal treatments was performed on 0.6-gram samples with 14.5 ml HNO<sub>3</sub>, 4 ml H<sub>2</sub>SO<sub>4</sub>, and 2 ml of HCl. All analyses were performed on Star 6 Plus System. The final volume of each sample was 100 ml. Samples were filtered (#41). The extracts were sent to WSRC, EPD, EMS Lab (735 B) for ICP -AES analysis. The samples were analyzed by Alex Guanlao (phone: 803-725-2432). SC DHEC Certification: 02550001

**Table 6C.** Total digestion of the sediment samples from the TNX OD; vertical and horizontal treatments.

Lab #	Sample ID	Treatment	Sample wt [g]	Final vol. of solution [ml]	Correction Factor	Vessel ID	Raw data P mg/kg	Final conc. P Mg/kg	Raw data Fe mg/kg	Final conc. Fe mg/kg
Vertical Treatments										
1	blank 1					23	0.527		0.3444	
	blank 2						1.964		0.05689	
2	V-control-IIa	Vertical – Control	0.5939	100	168.4	5	2.906	489.3	46.3	7796
3	V-control-IIb	Vertical – Control	0.6010	100	166.4	18	3.779	628.8	43.39	7220
4	V-control-IIc	Vertical – Control	0.6080	100	164.5	12	3.678	604.9	44.53	7324
5	V-control-Ia	Vertical – Control	0.6059	100	165.0	2	2.502	412.9	38.86	6414
6	V-control-Ib	Vertical – Control	0.6015	100	166.3	6	2.826	469.8	37.14	6175
7	V-control-Ic	Vertical – Control	0.6071	100	164.7	21	2.648	436.2	40.1	6605
8	V-NCA-Ia	Vertical – NCAI	0.5955	100	167.9	4	12.09	2030.2	37.1	6230
9	V-NCA-Ib	Vertical – NCAI	0.5966	100	167.6	17	8.414	1410.3	35.24	5907
10	V-NCA-Ic	Vertical – NCAI	0.6006	100	166.5	14	4.318	718.9	35.33	5882
11	V-NCA-IIa	Vertical – NCAII	0.6074	100	164.6	61	3.329	548.1	26.55	4371
12	V-NCA-IIb	Vertical – NCAII	0.6053	100	165.2	18'	2.759	455.8	19.23	3177
13	V-NCA-IIc	Vertical – NCAII	0.5994	100	166.8	4	2.368	395.1	23.04	3844
14	V-BA-Ia	Vertical – BAI	0.596	100	167.8	23	20.58	3453.0	45.61	7653
15	V-BA-Ib	Vertical – BAI	0.5988	100	167.0	17	15.52	2591.9	43.36	7241
16	V-BA-Ic	Vertical – BAI	0.6087	100	164.3	2	9.254	1520.3	32.43	5328
17	V-BA-IIa	Vertical – BAI	0.5962	100	167.7	61	14.75	2474.0	35.93	6027
18	V-BA-IIb	Vertical – BAI	0.6069	100	164.8	21	6.972	1148.8	35.7	5882
19	V-BA-IIc	Vertical – BAI	0.5924	100	168.8	18'	3.428	578.7	39.97	6747
20	V-Fe-Ia	Vertical – FeI	0.6043	100	165.5	8	3.407	563.8	58.23	9636
21	V-Fe-Ib	Vertical – FeI	0.6067	100	164.8	9	3.453	569.1	35.09	5784

22	V-Fe-Ic	Vertical – FeI	0.6084	100	164.4	14	3.385	556.4	33.48	5503
23	V-Fe-IIa	Vertical – FeII	0.6066	100	164.9	12	3.934	648.5	104.4	17211
24	V-Fe-IIb	Vertical – FeII	0.5997	100	166.8	5	4.133	689.2	66.54	11096
25	V-Fe-IIc	Vertical – FeII	0.5997	100	166.8	6	3.863	644.2	64.67	10784
Horizontal Treatments										
1	H-BA/Fe-IA	Horizontal - BA/FeI	0.6055	100	165.2	2	5.237	864.9	57.15	9438
2	H-BA/Fe-IB	Horizontal - BA/FeI	0.5904	100	169.4	14	4.141	701.4	38.09	6452
3	H-BA/Fe-IC	Horizontal - BA/FeI	0.597	100	167.5	5	4.084	684.1	41.26	6911
4	H-BA/Fe-ID	Horizontal - BA/FeI	0.6068	100	164.8	61	3.224	531.3	32.81	5407
5	H-BA/Fe-IE	Horizontal - BA/FeI	0.6093	100	164.1	12	2.898	475.6	28.74	4717
6	H-NCA/Fe-IA	Horizontal - NCA/FeI	0.592	100	168.9	21	9.943	1679.6	70.09	11840
7	H-NCA/Fe-IB	Horizontal - NCA/FeI	0.5932	100	168.6	8	5.324	897.5	59.68	10061
	H-NCA/Fe-IC	Horizontal - NCA/FeI	0.6028	100	165.9	8	5.585	926.5	61.83	10257
	H-NCA/Fe-ID	Horizontal - NCA/FeI	0.608	100	164.5	23	4.846	797.0	70.9	11661
	H-NCA/Fe-IE	Horizontal - NCA/FeI	0.6044	100	165.5	9	4.333	716.9	62.15	10283
	H-BA-IA	Horizontal – BAI	0.5933	100	168.5	5	41.71	7030.2	57.04	9614
	H-BA-IB	Horizontal – BAI	0.5992	100	166.9	12	8.794	1467.6	48.26	8054
	H-BA-IC	Horizontal – BAI	0.6048	100	165.3	2	6.916	1143.5	31.78	5255
	H-BA-ID	Horizontal – BAI	0.6093	100	164.1	17	2.593	425.6	22.09	3625
	H-BA-IE	Horizontal – BAI	0.6039	100	165.6	8	2.217	367.1	25.29	4188
	H-NCA-IA	Horizontal - NCAI	0.6032	100	165.8	61	46.05	7634.3	43.79	7260
	H-NCA-IB	Horizontal - NCAI	0.6029	100	165.9	23	4.616	765.6	54.56	9050
	H-NCA-IC	Horizontal - NCAI	0.5963	100	167.7	21	4.393	736.7	37.62	6309
	H-NCA-ID	Horizontal - NCAI	0.5923	100	168.8	6	5.11	862.7	52.02	8783

H-NCA-IE	Horizontal - NCAI	0.6091	100	164.2	18	3.555	583.6	37.71	6191
H-Fe-IA	Horizontal - Fe(0)I	0.6084	100	164.4	14	7.494	1231.8	213.9	35158
H-Fe-IB	Horizontal - Fe(0)I	0.5924	100	168.8	9	6.922	1168.5	125.3	21151
H-Fe-IC	Horizontal - Fe(0)I	0.6049	100	165.3	6	6.416	1060.7	107.2	17722
H-Fe-ID	Horizontal - Fe(0)I	0.6099	100	164.0	17	5.568	912.9	91.68	15032
H-Fe-IE	Horizontal - Fe(0)I	0.6098	100	164.0	21	5.9	967.5	76.01	12465
H-Control-IIA	Horizontal - Control II	0.5983	100	167.1	5	5.274	881.5	50	8357
H-Control-IIB	Horizontal - Control II	0.599	100	166.9	2	6.689	1116.7	67.12	11205
H-Control-IIC	Horizontal - Control II	0.5991	100	166.9	14	6.855	1144.2	72.31	12070
H-Control-IID	Horizontal - Control II	0.601	100	166.4	4	4.966	826.3	82.1	13661
H-Control-IIE	Control II	0.6058	100	165.1	18	4.467	737.4	77.74	12833
Blank I					18"	1.817		0.04491	
Blank II					18	1.869		0.03024	

**Table 7C.** The results from a total digestion of the sediment samples from the TNX OD; vertical treatments.

Vertical Treatments	P - AVG mg/kg	P - STDEV	Fe - AVG Mg/kg	Fe - STDEV
V-control-a	451	54	7105	977
V-control-b	549	112	6697	739
V-control-c	521	119	6965	508
V-NCA-a	1222	1144	5301	1314
V-NCA-b	940	665	4542	1930
V-NCA-c	578	200	4863	1442
V-BP-a	1289	1048	6840	1150
V-BP-b	933	675	6562	961
V-BP-c	557	229	6037	1004
V-Fe-a	2001	2054	13423	5356
V-Fe-b	1524	1510	8440	3756
V-Fe-c	958	796	8143	3734
P-background	561	86	6101	1272

V - vertical, BP - Biological Phosphate, NCA - North Carolina Apatite, Fe - Fe(0)  
a, b, c - distance from P/Fe source (amendment) in cm: a- 0 to 1cm, b- 1 to 2cm, and c - 2 to 3 cm

**Table 8C.** The results from a total digestion of the sediment samples from the TNX OD; horizontal treatments.

Treatments	Concentration of P				
	Mg/kg	Mg/kg	mg/kg	mg/kg	mg/kg
	Distance				
	0-1 cm	1-2 cm	2-3 cm	3-4 cm	4-5 cm
H-control	881	1117	1144	826	737
H-Fe	1232	1168	1061	913	968
<b>P-background</b>	<b>1057</b>	<b>1143</b>	<b>1102</b>	<b>870</b>	<b>852</b>
H-BP	7030	1468	1144	426	367
H-NCA	7634	766	737	863	584
H-BP/Fe	865	701	684	531	476
H-NCA/Fe	1680	898	927	797	717
	Fe	Fe	Fe	Fe	Fe
	Mg/kg	Mg/kg	mg/kg	mg/kg	mg/kg
H-control	8357	11205	12070	13661	12833
H-BP	9614	8054	5255	3625	4188
H-NCA	7260	9050	6309	8783	6191
<b>Fe-background</b>	<b>8410</b>	<b>9436</b>	<b>7878</b>	<b>8690</b>	<b>7737</b>
Fe-background (stdev)	1178	1611	3668	5018	4525
H-Fe	35158	21151	17722	15032	12465
H-BP/Fe	9438	6452	6911	5407	4717
H-NCA/Fe	11840	10061	10257	11661	10283

H- horizontal, BP - Biological Phosphate, NCA - North Carolina Apatite, Fe - Fe(0)  
 Distance from P/Fe source (amendment) in cm